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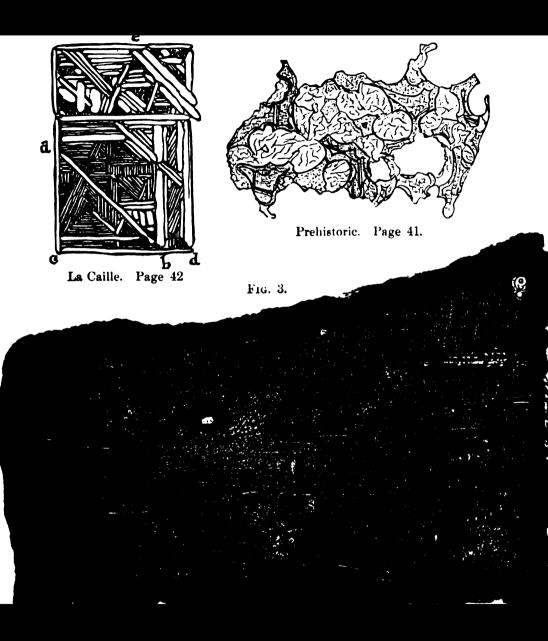
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# Proceedings of the American Academy of Arts and Sciences

American Academy of Arts and Sciences

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W. G. FARLOW.



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## **PROCEEDINGS**

OF THE

AMERICAN ACADEMY OF ARTS AND SCIENCES.

## **PROCEEDINGS**

OF THE

## AMERICAN ACADEMY

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### PROCEEDINGS

OF THE

### AMERICAN ACADEMY

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### ARTS AND SCIENCES.

VOL. XXIII.

PAPERS READ BEFORE THE ACADEMY.

Investigations on Light and Heat, made and published wholly or in part with Appropriation from the Rumpord Fund.

I.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

OXYGEN IN THE SUN.

By John Trowbridge and C. C. Hutchins.

Presented March 9, 1887.

SINCE the time when it was announced that hydrogen existed in great abundance in the sun's atmosphere and was a controlling element in its economy, there have been no more interesting questions in solar physics than those touching the presence of other gases in the sun's body and atmosphere; and when we consider the important part that oxygen plays in terrestrial affairs, the great variety of combinations into which it enters, and its high constituent percentage in the composition of the earth itself, a peculiar interest, second to that of no other element perhaps, attaches to its probable presence in the sun.

The investigation of the spectrum of oxygen as a research by itself, and as connected with its presence in the sun, has occupied many eminent physicists; but the fact that the latest and most complete investigations have left the minds of scientific men still in doubt has led the writers to take up the question again with more perfect and powerful apparatus and increased facilities, in order if possible to add something to the knowledge of the subject.

VOL. XXIII. (N. S. XV.)

The question of the existence of oxygen in the sun was first seriously investigated, we believe, by Dr. Henry Draper, who published in the American Journal of Science for 1877 and 1879, and in foreign journals, papers accompanied by reproductions of his photographs. Dr. Draper was firmly persuaded of the existence of oxygen in the sun's atmosphere, and based this belief upon the apparent coincidence of the lines of oxygen taken in air with certain bright spaces in the sun's spectrum which appeared upon his photographs.

Prof. John Christopher Draper published a paper in the American Journal of Science for 1878, in which he stated his conviction that oxygen exists in the sun; but his line of argument was just the reverse of that of Dr. H. Draper. While the latter apparently proved the existence of oxygen in the sun by the coincidence of its bright lines with bright spaces in the solar spectrum, the former was led to believe that the bright oxygen lines coincided with dark lines in the sun.

Both observers abandoned the old method of eye observation, and took advantage of the improvements in photography to record the oxygen lines upon a sensitive plate. Dr. H. Draper was led to abandon Geisler's tubes filled with oxygen, and to employ the electric spark in common air, on account of the greater brilliancy of the lines, while Prof. J. C. Draper still adhered to tubes filled with rarefied oxygen. The oxygen lines had been mapped by previous observers, notably by Thalen, and Schuster had shown that there were four spectra of oxygen which could be produced under varying conditions of temperature and pressure.

The photographs of Dr. Henry Draper's oxygen spectrum, together with the juxtaposed solar spectrum, were submitted to the French Academy of Sciences in Paris, June 23, 1879, by M. Cornu. From the remarks of M. Faye we make the following extract:—

"Dr. H. Draper has, however, succeeded in discovering oxygen, not in the chromosphere, but in the photosphere, where it discloses itself by bright lines. It is obvious that this gas is dissociated at a depth, and is immediately taken up by multiple combinations in the region and at the temperature of the brilliant surface. I see in these facts the hope of a confirmation, and above all of an extension, of the views I have put forth on the constitution of the sun; but whatever may be the fate that the progress of spectrum analysis reserves to them, I express here my admiration for the discovery of Mr. Draper, and I hope that his results, so well confirmed by the photographic proofs that our learned member, M. Cornu, has shown the

Academy, will not delay in being universally accepted by competent judges."

The opinion thus expressed by so eminent an authority as M. Faye testifies to the strength of the evidence brought forward by Dr. Draper. With the exception of Prof. John C. Draper, physicists, in so far as they have expressed their views, have generally accepted the hypothesis of Dr. Draper. No one, to our knowledge, has critically examined the hypothesis of bright lines in the solar spectrum.

The reader of Dr. H. Draper's account of his experiments will remember the difficulties he encountered in obtaining an air spectrum of sufficient brightness to record itself upon the photographic plate. The time that has elapsed since his work does not seem to have made those difficulties less, and, in spite of all our ingenuity has been able to devise, we have been practically confined to taking the spark in free air or oxygen at atmospheric pressure, notwithstanding the broad and hazy character of the lines under these conditions.

Not to record a long list of failures extending over several months, we will briefly describe the arrangements in their final form.

An alternating current dynamo driven at 2,000 revolutions per minute is connected to a commutator of four segments upon a fixed spindle, around which revolve two pairs of brushes. The result of this combination is that the current is very frequently and sharply interrupted. This interrupted current is used to excite three large quantity coils connected in series. From two to twelve jars were employed as a condenser to the secondary current. The spark was taken between two stout rods of aluminium placed immediately in front of the slit, and the spark passed between them with a deafening rattle, and gave about the light of two candles. We tried Dr. Draper's device of a soapstone compressor for the spark, but in our hands the walls of the soapstone near the spark melted down, and formed a conducting surface over which the current passed.

The photographic apparatus is the large instrument of Professor Rowland,—a concave grating with ruled surface  $6\times 2$  inches, mounted upon an iron girder 23 feet long, moving upon two tracks at right angles, as has been previously described by him and others. Sunlight is introduced by a heliostat with mirror silvered on first surface, and an image of the sun formed on the slit by means of a quartz lens of five feet focus. The method of working with the apparatus so arranged has been as follows.

The points of aluminium being permanently fixed in front of the alit, sunlight is introduced, the camera brought to focus once for all,

and set to any required wave-length upon a convenient scale. photographic plate is then placed in the camera, and a shutter immediately in front is set to expose the upper half of the plate. Exposure for the sun is then made; the sunlight is then cut out, and the shutter moved to cover that part of the plate already exposed, and the lower half exposed. The spark is then started and worked from 15 to 30 minutes. In addition to the spectrum of lines there is a considerable continuous spectrum, which after a time causes fogging of the plates; so there does not seem to be any gain in an exposure of more than half an hour. The feebleness of the air lines can be judged of when we state that, with the same plate, breadth of slit, etc., we get a metallic spectrum in the arc in ten seconds, strongly There was sufficient iron present in the electrodes as photographed. impurity to give the strongest iron lines feebly, and these have been of use in determining that no displacement had happened, although from the nature of the arrangements such disturbance could hardly occur.

On the negative produced as above indicated the two spectra lie exactly edge to edge, like a vernier and scale, and are in the best possible position for the accurate determination of the position of the air lines. The original plan contemplated a determination of wave-lengths of all the air lines throughout the entire spectrum; but persistently bad weather and other causes have compelled the post-ponement of the completion of this work, though ware now able to give it complete from wave-length 3740 to wave-length 5030.

The photographic map of the solar spectrum of Professor Rowland has made easy what would otherwise have been an undertaking of extreme labor and difficulty. The best of engraved maps of the violet region of the spectrum to beyond F are comparatively worthless. Even on the elaborate map of Vogel, the result of years of labor, it is difficult certainly to recognize other than the more prominent lines, and you never feel quite sure of your positions; but we turn to the map of Rowland with the certainty of finding every line in its true order and magnitude, so that what was formerly most difficult has now become very simple, and the position of any well-defined air or metallic line can be read directly, by comparison of the photograph with the map, to the tenth of a wave-length.

We here give a table of wave-lengths as determined from our photograph of the sun and air spectra:—

a=40.00 G.	. 4107.01	0.	4000 07	77 #-1A
8749.80 Strong, agrees.	4105.21	Strong.	4330.87	Very faint.
3755 35 " "	4109.76	Very strong.	4881.20	O1
3830.60 Faint and broad.		Very faint	4332.40	Sharp.
8839.275 Dim and broad.	4112.16		4386.77	α.
8842.30 Very faint.	4119.86	Fairly strong.	4845.52	Strong.
9010,00	4120.46	Faint.	4347.47	Faint.
3850.70 Faint.	4121.52	4	4347.94	Strong.
8857.40 <b>"</b>	4121.56	. "	4849.30	"
8863.80 "	4123.82	Agrees.	4351.40	"
8864.90 "	4132.82	Faint.	4353.70	4
3882.45 Strong.	4133.79	**	4856.62	Faint.
3893.50 Faint.	4145.87		4862.90	
8894.95 <b>"</b>	4147.42		4365.40	Faint.
8896.40 "	4151.92		4366.92	Strong.
8896.90 "	4158.57	May agree.	4869.60	Faint.
8900.975 Sharp.	4155.42	Faint.	4371.40	4
8902.20 Very faint.	4156.79		4379.70	44
8906.00 Sharp.	4164.72	Faint.	4381.50	"
8912.30 Fairly strong.	4166.72	"	4385.30	Very faint.
3919.25 Strong, agrees.	4169.47	Agrees.	4885.40	
8935.10 Very taint.	4172.12		4386.50	Nebulous.
8936.90 Faint.	4175.72	Band.	4396.30	Faint.
<b>3938.80 "</b>	4177.92	Very faint.	4401.22	
<b>893</b> 9. <b>80</b> "	4179.92	Faint band.	4415.00	Strong, agrees.
8940.70 "	4185.82	Very strong.	4417.17	4 4
8941.40 "	4190.00		4421.00	Faint.
8942.48 Sharp.	4193.77	Very faint.	4426.00	4
8946.20 " <sup>-</sup>	4198.72	•	4430.04	4
8948.10 Very faint.	4199.22	May agree.	4431.90	Very broad dim
8949.00 { Sharp, may	4202.12	" " "		band.
8949.00 agree.	4205.72	Very faint.	4434.27	Sharp.
8951.45 "	4206.92	Band.	4439 47	Broad dim band.
8954.85 Strong.	4209.12	Very faint.	4443.00	4 4
8956.175 Strong agrees.	4214.92	""	4447.09	Very strong.
3958.10 Faint.	4223.17	Faint on band.	4452.40	Sharp.
<b>3958.90</b>	4224.92	4 4	4456.00	Faint and sharp.
8959.975 Sharp.	4225.92	" "	4459.90	Faint.
<b>39</b> 63.70 "	4228.52	Band.	4465.40	Sharp.
<b>3968.70</b>	4236.67	u	4466.00	"
3973.60 Strong.	4241.92		4468.02	Very faint.
8981.40	4249.02		4469.50	46
8982.97 Faint.	4258.42	Very faint.	4472.90	"
3992.87 Sharp, agrees.	4266.32	Faint.	4477.87	Broad and faint.
8995.10 Very strong.	4271.22	66	4481.87	Sharp.
( Vory faint may	4274.82	Very faint.	4487.94	•
8998.81 agree.	4277.90	Faint.	4489.90	Faint.
4008.89	4279.90	Fairly strong.	4496.97	Sharp.
4011.84 Faint.	4282.40	Faint.	4498.95	Faint.
4085.34 Band.	4291.90	44	4503.05	Fairly strong.
4041.89 Band.	4303.80	Very faint.	4507.72	u
4066.84 Faint.	4805.67	4	4511.85	Sharp.
4070.24 Strong, may agree.	4309.87	Faint and sharp.		0
4070.24 agree.	4812.72	4 4	4520 50	agree.
4072.34 "	4815.52	4 4	4544.50	Fairly strong.
4076.19 "	4817.20	Strong.	4565.97	Sharp.
4078.83 Faint, agrees.	4819.50	4	4572.02	Sharp, agrees.
4085.24		Faint, may	4577.50	Sharp.
4085.84	4822.80	agree.	4578.55	4
4098.64 Faint.	4828.90	Very faint.	4582.32	«
4093.09 "	4325.90	Agrees.	4583.15	Very strong.
4097.49 "	4327.60	Very faint.	4587.45	Sharp.
4105.04 Strong.	4828.42	"	4588.05	a P.
	, ~~~~~			

4588.92 Very faint.	1 4682.40	Very faint.	4842.00	Faint but sharp.
4589.40 "	4687.15	"	4863.92	"
4590.00 "	4688.80	44	4877.70	Faint.
4500 05 Strong, may	4691.40	4	4878.80	Very faint.
4590.95 agree.	4694.15	Strong.	4879.90	"
4592.00 `	4695.15	Faint.	4591.27	u
4592.95 Strong.	4696.70	Very faint.	4894.90	u
4596.20 "	4699.40	Broad and faint.	4898.70	"
4601.37 Very strong.	4700.40	Faint.	4906.77	44
4607.20 "	4701.65	u	4907.67	"
4609.45 Sharp, may	4703.02	Agrees.	4913.69	Sharp.
( agree.	4705.42	Fairly strong.	4915.12	Sharp, but faint.
4612.75 Faint.	4710 20		4916.86	Sharp.
4614.05 Strong, agrees.	4712.87	Very faint.	4936.86	Band.
4621.42 Strong.	4719.92	4	4940.85	Sharp.
4630.73 Very strong.	4781.27	"	4945.01	44 -
4684.00 Sharp.	4733.95	"	4945.81	44
4638.90 Strong.	4740.20	4	4950.21	"
4640.75 Rather faint.	4744.20		4951.41	Nebulous band.
4641.90 Fairly strong.	4753.82	Sharp.	4953.85	Sharp, agrees.
4643.45 Strong.	4760.07	"	4955.16	
4645.40 Faint.	4768.82	ii l	4960.13	
4649.25 Strong.	4771.82		4969.85	
4651.02 Fairly strong.	4775.07		4972.85	
4654.10 Faint.	4782.62	Very strong.	4979.90	01
4654.85 "	4788.27	Very faint.	4983.06	Sharp, may
4655.00 Faint band. 4658.05 Very faint.	4791.82	Sharp, agrees.	4993.95	agree.
4658.05 Very faint. 4659.60 "	4798.97 4800.82	Very faint.	4997.60	Faint.
4665.70 Faint.	4802.87	Varratrona	4999.81	A
4667.55 "	4808.94	Very strong. Very faint.	5001.55	Agrees. Faint.
4671.65 "	4810.02	Faint.	5011.06	Sharp, agrees.
4672.80 "	4811.92	rame.	5012.50	Faint.
4678.80 Very faint.	4818.52	u	5012.55	May agree.
( Faint man	4816.60	Very strong.		Faint, may
4674.95 } Failt, thay agree.	4820.90	Faint.	5022.95 }	agree.
4676.40 " "	4822.12	4	5033.85	Very faint.
4681.10 Very faint.		Faint, may agree.		· ·· · · · · · · · · · · · · · · · · ·

In regard to the accuracy that may be expected of the above positions, we feel sure that few of them are wrong by more than a tenth of a wave-length, and those are of the class "Very faint," or "Broad and nebulous." The better defined lines we believe to be correct to within less than the above amount. The method of comparison we have used admits of much greater accuracy than this, but the ill-defined character of the air lines puts a limit to their accurate placing. Compared with Thalen's positions, they should be credited with ten times the accuracy at least. Some of Thalen's bands are resolved into two or more in our instrument.

Prof. John C. Draper projected his spectra upon a scale of wavelengths by means of a stereopticon, — a method which does not inspire confidence in his results, when we consider the distortion produced by projecting lenses.

The scientific world seems largely to have accepted the wave-lengths of Ängstrom and Thalen as final. One eminent authority speaks of them as the "ne plus ultra" of spectroscopic accuracy; and any attempt to revise or correct them may be looked upon as presumptuous. However, we believe the time has arrived when the whole of Thalen's work on metallic spectra must be re-examined. It is safe to say that he has tabulated not more than one line in many metals where several exist, and his positions are occasionally wrong by as much as two wave-lengths.

As yet no approach to the accuracy with which the solar spectrum has been delineated has been attempted in metallic spectra,—a remarkable fact, when we consider that the chief interest that attaches to the study of the solar spectrum is in its connection with spectra of terrestrial elements.

The test of the existence of oxygen in the sun is the coincidence of the bright lines of the spectrum of oxygen with bright lines or with dark lines of the solar spectrum. If the bright lines of any metallic vapor formed in the electric arc or the electric spark coincide with the dark lines of the solar spectrum which is photographed directly above the spectrum of the metal on the same sensitive plate, the evidence is usually considered conclusive in regard to the existence of the metal in the sun. In the case of iron, where hundreds of lines of the metal coincide with dark lines in the solar spectrum, not only in exact position but in general grouping and character, the evidence cannot be doubted by any one who has carefully examined it. When a majority of the lines of any metal coincide with dark lines in the solar spectrum under high dispersion, not only in position but in grouping, while a few of the metal lines have no representatives in the solar spectrum, there is a probability that the corresponding lines wanting in the sun have been obliterated by superposed lines or bands of other metals. In our paper "On the Existence of Carbon in the Sun," we have called attention to a case of such obliteration. It is probable, also, that the non-appearance of certain lines in the sun may be due to certain conditions of temperature. We have discussed this point more fully in the paper on Carbon, above referred to.

The same remarks apply to the coincidence of the lines of any element with the supposed bright spaces in the sun. The value of the test of coincidence increases with the number of coincidences. If an element has only two or three lines, and these two or three agree in position with dark lines in the solar spectrum, the evidence of the

existence of the element in the sun is not conclusive. It is supported, however, if there is any striking peculiarity in the lines of the element which is reproduced in the corresponding lines in the solar spectrum. Thus the nebulous character of the lines of magnesium is perfectly reproduced in the corresponding lines in the solar spectrum. The test of coincidence, therefore, requires primarily a normal spectrum and the highest possible dispersion. The earlier observers were limited to instruments of small dispersion, and the entire number of lines observed in the solar spectrum was small compared with that given by the best modern apparatus. The chances for an apparent coincidence were therefore much greater, and evidence of a very misleading character could be obtained.

In Dr. H. Draper's published photograph, the coincidence of the greater part of the oxygen lines with bright bands in the solar spectrum is quite striking; and it is not a matter of surprise that he was led to conclude the connection between the two spectra to be a physical one, and to announce the existence of oxygen in the sun as proved. Instances are not infrequent where instrumental imperfection or lack of power has led to results unsupported by later and more powerful research. Witness the spots of Venus of the older observers. Now when we apply to the spectra of the sun and oxygen a dispersion and definition that show the minute detail of each, the "bright bands" at once vanish, or no longer appear as such, and all the apparent connection between them and the oxygen lines disappears also. The bright bands of Dr. H. Draper's spectrum are found to be occupied by numerous dark lines, of various degrees of intensity; but the hypothesis of Prof. J. C. Draper, that these are the true representatives of the oxygen lines, is rendered untenable by the lack of any systematic connection between the two. It happens quite frequently that an oxygen line falls centrally upon the space between two dark lines of the solar spectrum, but not more frequently than we might expect as a matter of chance, when we consider the vast number of lines and spaces; and the fact that the spaces are no brighter than the surrounding background of the solar spectrum would not seem to permit of their interpretation as bright lines.

The subject of bright lines in the solar spectrum is one upon which men will probably differ, and we have sought information upon it. Of course there is no a priori reason why such bright lines should not exist, as they do in many stars; but we have photographed the sun's spectrum every day that the sun has shone for nearly five months, without finding a line that could with certainty be pronounced

brighter than its neighbors; and it must be admitted that the photograph is the best of photometers in such a case.

In regard to the other three spectra of oxygen of Schuster we have nothing to say; but as far as concerns the spark spectrum in air and the solar spectrum from wave-lengths 3749.8 to 5033.85 we can safely affirm that there is no physical connection between them.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

#### II.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

ON THE EXISTENCE OF CARBON IN THE SUN.

By John Trowbridge and C. C. Hutchins.

Presented March 9, 1887.

From the presence of absorption bands in the solar spectrum at high altitudes, Captain Abney has been led to believe in the existence of certain hydrocarbons between the earth and the sun; and Siemens's theory of the conservation of solar energy depends upon the supposed existence of carbon vapor in interplanetary space. It is not our purpose to discuss Abney's observations, or the truth of Siemens's hypothesis. We wish to call attention to the remarkable character of the carbon spectrum, formed by the Voltaic arc in air between carbon terminals; and to draw attention to the evidence presented by the juxtaposed solar spectrum of the existence of carbon in the sun.

In our early experiments the carbon terminals between which the Voltaic arc was formed were heated several hours, while a stream of chlorine gas was passed over them. This operation was not entirely successful in removing metallic impurities. Subsequently we discovered that the spectra of these impurities could be readily distinguished from the marked fluted carbon spectrum, and we therefore employed the ordinary compressed carbon sticks employed in electric lighting.

For our work the nicest adjustment of slit was necessary, in order that no displacement of spectrum lines could possibly occur when the carbon spectrum was photographed in juxtaposition with the solar spectrum. This was accomplished by the use of a slit, the jaws of which opened equally.

One of Rowland's concave gratings, of 21 feet 6 inches in curvature and 14,000 lines to the inch, was employed. In order to avoid any possible displacement of the photographic camera during the operation of photographing the carbon spectrum immediately below the solar

spectrum, a drop shutter was arranged directly in front of the sensitive plate, the movement of which was independent of any movement of the camera. Preliminary experiments showed us the importance in this work of employing a spectroscope of great dispersion and of fine definition, giving also a normal spectrum. The use of a prism spectroscope would undoubtedly have masked the phenomenon we have observed. For our purposes, therefore, Rowland's apparatus was peculiarly advantageous.

Our experiments lead us to conclude that there is positive evidence in the solar spectrum of the existence of carbon in the sun. Before giving an account of our experiments in detail, a few observations may not be considered out of place.

One who studies the solar spectrum by itself, and who has had no experience in the formation and observation of metallic spectra, is apt to regard the dark lines in the solar spectrum as fixed in character and condition. A line which is seen by one observer, and not by another, is generally regarded as a terrestrial line formed by absorption in the earth's atmosphere. Certain lines are well known to be due to the terrestrial absorption, as can be easily proved by their appearance when the sun is observed at sunset, when the rays of light have to penetrate a greater thickness of the earth's atmosphere than at midday. The shifting layers of vapor in the sun's atmosphere also may, in certain cases, obliterate or strengthen certain lines of a metal. To understand this it is only necessary to extend the reasoning of the conservation of energy to the subject. It is a common lecture experiment to reverse the metallic lines by passing the rays of light produced by the vapor of the element through a layer of vapor colder than that of the source of the rays. The energy of the rays is thus absorbed in heating the colder layer. When the temperature of the vapor is increased, and becomes equal to that of the source, no reversal takes place. Thus, on the sun's surface the conditions for a reversal may be wanting at certain times, and faint lines may become bright. Their brightness may not be sufficient to affect the general illumination of the solar spectrum of which they form a part. may arise, moreover, in which the temperature of the reversing vapor may be called critical, — at such a temperature that the faint reversal is sufficient to extinguish the bright line of a metal without producing a well-defined dark line. At certain epochs, also, the temperature of the vapor of any element in the sun may be higher than at other times; and certain lines may thus appear which are wanting when the temperature falls. One is forced to these conclusions in observing the conditions under which the varying character of metallic spectra are produced. For instance, we have caused the rays from iron vapor to traverse a long and dense layer of iron vapor, and have observed that the strength of the lines and the number of reversals have been largely increased. In another experiment, the lower carbon of the electric lamp we employed occupied the centre of an electro-magnet. This was accomplished by passing the carbon through a hollow iron cone, and surrounding the latter by layers of wire, through which the electrical current employed in generating the light passed. In this case the electric arc was spread out at right angles to the pole of the magnet, into a fan-like, intensely hot flame, which roared loudly, and which rarefied, so to speak, the iron vapor between the carbon terminals. The strength of the lines and the number of reversals were diminished under this new condition.

Another phenomenon may happen. When an excess of the vapor of one metal floats over or is mixed with that of another, the lines of one metal are superimposed upon those of another in the solar spectrum, and the stronger spectrum of one element may easily obliterate the weaker spectrum of another. Thus we have succeeded in completely obliterating the fluted spectrum of carbon in the green and blue, by photographing upon it the spectrum of iron, of nickel, and of cerium. A species of composite photograph was thus obtained. It is possible that in the future Galton's ingenious method of composite photography may be applied to the solar spectrum; and by a judicious selection of photographs of the elements, a composite photograph may be obtained which will closely resemble portions of the solar spectrum, and will enable us to judge of the composition of the reversing layers of the sun.

To the varying conditions which we have thus outlined are due, we believe, the disappearance in the sun's spectrum of the marked fluted spectrum of carbon in the green and blue portions.

A careful examination of the fluted spectrum of carbon, however, with the juxtaposed solar spectrum, discloses a remarkable fact: while traces of obliteration of the evidence of carbon vapor are seen, yet the general character of the lines in the solar spectrum immediately juxtaposed with the fluted spectrum of carbon near H lead us to believe that there is unmistakable evidence of the existence of carbon vapor in the sun. When the arrangement of the fine lines of the spectrum of carbon is plotted as a curve, and that of the dark lines in the solar spectrum immediately above the carbon spectrum is also plotted, the two curves have a remarkable similarity in character, running with a slight convexity toward one axis.

In the first fluting at wave-length 3883.7 within the limit of ten wave-lengths, over 28 of the spaces between the fine bright lines of the flutings coincide with dark lines immediately in juxtaposition in the solar spectrum. When we consider that the progressive arrangement of these lines is exactly the same both in the spectrum of carbon and that of the sun, we cannot consider that this coincidence is the result of chance. On examining the spectrum of carbon in the region near H still further, a remarkable number of coincidences of the spaces between the bright lines of the carbon spectrum with dark lines in the solar spectrum will be observed. We are led, therefore, to conclude that the fluted spectrum of carbon is an example of the reversal of the lines of a vapor in its own vapor. Fluted spectra occur at comparatively low temperatures. When carbon is ignited, we have at first a continuous spectrum. When the temperature increases and the carbon is volatilized, fluted spectra occur, which consist of interruptions of the continuous spectrum by fine line reversals occurring in harmonic order. The same phenomenon can be observed in the spectrum of iron lines: through the centre of an iron line, when a sufficient amount of iron vapor surrounds the Voltaic arc in which iron is volatilized, reversal lines are always seen. Now if the iron lines were arranged in regular order, the reversals would also be in like regular order, and would coincide with similar reversals in the solar spectrum. Assuming the conditions at the sun's surface to be the same as those we have in the Voltaic arc, when carbon is volatilized, the character of the carbon spectrum should exactly agree with the character of the solar spectrum juxtaposed. This is found to be true to a remarkable degree in comparing portions of the solar spectrum with portions of the fluted spectrum of carbon beginning at wave-length 3883.7.

Our hypothesis leads us to conclude, that, at the point of the sun's atmosphere where carbon is volatilized, so as to produce the peculiar arrangement of reversals observed, the temperature of the sun approximates to that of the Voltaic arc.

Investigations on Leght and Heat, made and published wholly or in part with Appropriation from the Rumpord Fund.

#### III.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

ON THE EXISTENCE OF CERTAIN ELEMENTS, TOGETHER WITH THE DISCOVERY OF PLATINUM, IN THE SUN.

BY C. C. HUTCHINS AND E. L. HOLDEN.

Presented by Professor John Trowbridge, March 9, 1887.

LATE in the fall of 1886 it was decided by the writers, who were then at work in the Physical Laboratory of Harvard University, to attempt a revision of some of the previous work in regard to the chemical constitution of the sun, as well as to discover, if possible, new facts bearing on the same subject. For the purpose of this investigation a magnificent diffraction grating, made by Professor Rowland of Baltimore, was kindly placed at our disposal by Professor John Trowbridge, under whose supervision and direction the subsequent work has been done.

After some delay caused by the mounting of the grating and its attachments, work was begun early in January, 1887, but, owing to bad weather and other hindrances, was not regularly and systematically prosecuted till somewhat later.

The grating used is of speculum metal with a ruled surface measuring 6 inches by 2, having 14,438 lines to the inch. It is concave, its radius of curvature being 21½ feet, and is mounted according to Professor Rowland's method. Suffice it to say, that the method is such that, by simply rolling the camera along an iron track, it passes not only from one part of the spectrum to another, but also to the spectra of different orders, at the will of the operator. As the distances on this track are proportional to the relative wave-lengths of the lines that fall successively on a given point in the camera, it is easy, by means of a suitable scale of equal parts placed beside the track, to set the centre of the photographic plate instantly within a single wave-length of any given line in the spectrum.

And here let us parenthetically state that all our wave-lengths are those given by Professor Rowland's photographic map of the solar spectrum, the position of every line referred to being carefully identified upon the map, and its absolute wave-length thus determined. Although some of the negatives contain many lines too faint to show on the map, yet we feel confident that our numbers correspond in all cases to those of the map within one tenth of a wave-length.

The light is brought into the room by means of a porte lumière, and then sent through the slit after total reflection by a right-angled prism. Before striking the prism it passes through a cylindrical lens, which condenses it to a band of light about 2 inches long and  $\frac{1}{8}$  inch wide. The jaws of the slit move equally in opposite directions, so that, however widely they may be opened, no lateral displacement of lines can result from this cause.

Directly in front of the slit is placed a large tin lantern containing an electric lamp; the image of the arc can be brought exactly upon the slit by means of an adjustable lens in the front of the lantern. In the lower carbon of the lamp is made a cup-shaped cavity, which is filled with the substance a spectrum of which is desired. It is not at all necessary that this be in the form of a metal, for any ordinary compound is at once reduced by the intense heat and the presence of carbon vapor to the metallic state.

The plan of working has been as follows. The apparatus being arranged as described, the sunlight is admitted and the desired portion of solar spectrum photographed upon the upper half of the plate; then the sunlight is excluded by a shutter, and the image of the electric arc containing the proper metal is allowed to fall upon the slit, and its spectrum photographed on the lower half of the plate. (Most of the plates used were those made by the M. A. Seed Co., and were cut to the size of 8 inches by 2. The most sensitive plates were obtained, and even then we found the required time of exposure for some parts of the spectrum inconveniently long.)

In order to effect the exposure of either half of the plate at will, we placed directly in front of the camera an opaque screen, in which was a rectangular opening one half the size of the plate. By turning a handle, this screen is raised or lowered without the slightest disturbance of camera or plate. The metallic spectrum, being thus photographed immediately below the solar spectrum, can be compared with it at leisure.

These spectra are then examined with the aid of a glass magnifying about ten diameters, and any coincidences between solar and metallic

lines carefully noted according to their wave-lengths. In order to eliminate any personal error, they are examined by both observers separately, and their results afterwards compared.

To eliminate errors arising from suspected impurities of materials, as also from the impurities known to exist in the carbons employed, we took what we called "comparison photographs." For these, we placed in the carbon cup a portion of the substances known or suspected to be present as impurities in our metal, and then photographed the spectrum thus given on the upper half of the plate; a piece of the metal under experiment was then placed in the lamp, and the spectrum photographed on the lower part of the plate. Any lines due to impurities would then extend entirely across the plate, while those of the pure metal would extend only half-way. In addition to this precaution we consulted all accessible tables and plates as to the position of known lines of metallic spectra, and also compared together all our photographs of the same region. If all of these tests left any doubt as to the origin of a given line, it was at once subjected to special investigation until all doubt was removed.

The dispersion given by the apparatus in the order of spectrum in which we worked is such that a single wave-length occupies on the negative a space of 1.12 mm. This makes the distance between the lines  $D_1$  and  $D_2$  6.7 mm., while the length of spectrum from A to H is about 4.1 m. With so great dispersion it would hardly be possible to mistake the position of a line by any very considerable amount, or to confound neighboring lines belonging to different metals.

For reasons readily apparent, it was found so difficult to photograph under high dispersive power those parts of the spectrum not lying between wave-length 3600 and wave-length 5000, that our photographic work was done chiefly within those limits. It was, however, supplemented in many cases by eye observations in other portions of the spectrum.

We are convinced that there is much in the whole matter of coincidences of metallic and solar lines that needs re-examination; that something more than the mere coincidence of two or three lines out of many is necessary to establish even the probability of the presence of a metal in the sun. With the best instruments the violet portion of the solar spectrum is found to be so thickly set with fine lines, that, if a metallic line were projected upon it at random, in many places the chances for a coincidence would be even, and coincidences could not fail to occur in case of such metals as cerium and vanadium which give hundreds of lines in the arc.

Moreover, a high dispersion shows that very few lines of metals are simple and short, but, on the contrary, winged and nebulous, and complicated by a great variety of reversal phenomena. A "line" is sometimes half an inch wide on the photographic plate, or it may be split into ten by reversals.

At first, we believed that these reversals were due to defects in the ruling of the grating, but we are convinced that they are true phenomena from the following experiments. 1st. The wings continue when various portions of the grating are covered. 2d. They are the same in three successive orders of spectra. 3d. They are very different in different metals, and in some are not seen at all. 4th. We arranged a flat grating, with collimator and projecting lens, each of five feet focus, and found that with this apparatus the same phenomena appeared.

On pages 87 and 88 of "The Sun," Professor Young gives a list of elements in the sun according to the best authorities, which is followed by a list of doubtful elements. Some of these we have examined with the following results:—

Cadmium. — The coincidence of the two lines given by Lockyer at wave-lengths 4677 and 4799 is perfect. These are the only cadmium lines near, and sun lines in the vicinity are not numerous.

Lead. — The evidence for lead, due to Lockyer, is based upon three lines at 4019.7, 4058.2, and 4061.8. We have photographed these lines with the sun many times. They are broad and nebulous, and often several times reversed. Lines in solar spectrum numerous and faint. 4019.7 and 4058.2 certainly do not coincide. 4061.8 is very difficult to pronounce upon; it may coincide.

Cerium, Molybdenum, Uranium, and Vanadium.— These four metals may be classed together. Lockyer finds four coincidences each for molybdenum and vanadium, three for uranium, and two for cerium. The arc spectrum of each is characterized by great complexity and vast numbers of lines. So numerous are the lines in fact, that often on the photographs the total space occupied by them is greater than the space not so occupied. A plate ten inches long may contain a thousand or so. Evidently coincidences between these and solar lines cannot fail to occur as matters of chance, and therefore prove nothing. One can easily count a hundred or so such coincidences without the slightest conviction that the connection is other than fortuitous. Of course all this is nothing against the probability of these metals being in the sun; but at the same time those peculiarities of grouping, strength of lines, and other characteristics which

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occur in the case of iron and other spectra, and which alone can serve as evidence in such cases, are conspicuously absent.

Among the metals whose existence in the solar atmosphere has seemed probable, we have examined the following:—

Bismuth. — The line of the above metal at 4722.9, the only line of bismuth in the arc in that whole region, coincides perfectly with the more refrangible of a very faint pair of solar lines.

Tin. — The solitary tin line at 4525, thought by Lockyer to coincide, falls directly between two fine lines in the solar spectrum.

Silver. — Lockyer mentions a certain possibility of silver in the solar atmosphere from the apparent agreement of two of its nebulous lines with solar lines. One of these we have never been able to find in the course of many photographs of the region in which it is given by him.

We find seven lines of silver between 4000 and 4900. Of these seven, three are what Thalen calls nebulous; so broad and hazy that their true positions cannot be determined with much accuracy. These lie at about 4055.5, 4063.6, and 4212. A fourth line at 4023 is of the same general character, but has a sharp reversal which agrees with a solar line. The remaining three lines are represented in the sun, and are given by Thalen in the spark spectrum of the metal.

4476.2. Very strong line; nebulous on lower edge. Sun line strong. (Thalen, 4475.)

4668.8. Strong, solitary line. (Thalen, 4666.5.)

4874.3. Fairly strong. (Thalen, 4874.)

Thus, between the limits given above, every line of silver, as far as can be determined, coincides with a solar line.

Potassium. — We could find but two lines of potassium, the same that were examined by Lockyer, 4044.5 and 4048.35. Each line is reversed four times, which increases the difficulty of locating them exactly. 4048.35 seems to agree with a solar line. The solar line near 4044.5 is very faint, and it is next to impossible to decide the question of an agreement.

Lithium. — The blue line of lithium presents a curious case. The very broad and nebulous line has a rather sharp reversal near the centre, and somewhat toward the lower edge a broader and less clearly defined reversal. Both these reversals agree with solar lines at 4602.5 and 4603.2. It is possible that one of the reversals may be due to the presence of some other substance, say calcium; but if that were true, it would seem that both reversals would be nearly, if not quite, obliterated. Further experiment may clear the matter up. 4603.2 is given to iron by Thalen.

Platinum. — As far as we can learn, no evidence has hitherto been offered to show the occurrence of this metal in the solar atmosphere. We were somewhat surprised, therefore, upon meeting with coincidences. Between 4250 and 4950 we find 64 lines of platinum, sixteen of which agree with solar lines. The latter are at the following places:—

4291.10	<b>4481.85</b>
4392.00 (Thalen 4389.4)	4552.80 (Thalen 4551.8)
4430.40	4560.30
4435.20	4580.80
4440.70	4852.90 (Thalen 4851.5)
4445.75 (Thalen 4442.0)	4857.70
4448.05	4899.00
4455.00	4932.40

We have taken all possible care to make this statement accurate, and to admit no lines about which there seemed to be any question. There are seven other lines not included in the list, the probability of agreement of which is at least as good as that upon which potassium is admitted.

In all these experiments everything has been done to bring out and show upon the photograph as much as possible. The lamp, constructed for the purpose and fed by a powerful dynamo, gave an arc from a half to three fourths of an inch long, and burned with a long flame and so intense a heat that it could be worked for but a few minutes at a time. Any one who has carried out a series of experiments like this is alone competent to appreciate the great labor and the endless difficulties and perplexities that attend them.

Our thanks are especially due to Dr. Wolcott Gibbs for his hearty encouragement, and for the use of valuable apparatus and chemicals.

### IV.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

## THE ACTION OF FLUORIDE OF SILICON ON ORGANIC BASES.

BY ARTHUR M. COMEY AND C. LORING JACKSON.

Presented June 15, 1887.

THE research described in the following paper was undertaken in the hope of obtaining from the amines products similar to the compound which ammonia gives with fluoride of silicon, (NH<sub>2</sub>)<sub>2</sub>SiF<sub>4</sub>, discovered by Gay-Lussac and Thenard,\* and three years later prepared and studied by J. Davy.† We have been able to find only two previous papers on this subject, one published by Laurent and Delbos,‡ in 1848, in which the action of fluoride of silicon on aniline is described, the product being a nearly white mass, which they washed with ether, boiled with alcohol, and sublimed to purify it for analysis; their analyses, however, led only to a very complex formula containing oxygen, which they advance "with much reserve," although it was confirmed by the proportions § in which its factors combined. The substance when treated with water gave a gelatinous precipitate of silicic acid, and when boiled with alcohol was converted into small white lustrous scales. The second paper was published by W. Knop,\*\* in 1858, and had for its primary object the study of the solution of fluoride of silicon in absolute alcohol, which gave with urea and aniline the fluosilicates of these bases, both of which Knop sublimed, and obtained from

<sup>\*</sup> Mém. d'Arcueil, ii. 817.

<sup>†</sup> Phil. Transact., 1812, p. 852.

<sup>†</sup> Ann. Chim. Phys., ser. 3, xxii. 101.

<sup>§</sup> These proportions agree tolerably with the formula worked out by us for this substance, but their analytical results do not, and are entitled to no consideration, on account of the difficulties in the analysis, which Laurent and Delbos did not succeed in overcoming.

Aniline fluosilicate.

<sup>\*\*</sup> Chem. Centralblatt, 1858, p. 388.

the urea fluosilicate only ammonic fluosilicate, silicic acid, and cyanuric acid; but from the aniline fluosilicate a new substance, which gave a precipitate of gelatinous silicic acid with water, and contained more silicon and fluorine than the fluosilicate. He did not, however, identify it with the substance made by Laurent and Delbos. We may add, that some years later W. Knop and W. Wolf \* describe the aniline fluosilicate more in detail.

The results of our work on this subject may be summarized briefly as follows. Aniline forms with fluoride of silicon a compound having the formula  $(C_6H_5NH_2)_3(SiF_4)_2$ , which sublimes without alteration, but is decomposed with water forming aniline fluosilicate and silicic acid; when heated with an excess of aniline it is converted into another compound having the formula  $(C_6H_5NH_2)_4(SiF_4)_2$ , and the same substance is formed when fluoride of silicon acts on aniline at high temperatures. This second product is unstable, breaking up spontaneously into the first and free aniline. The following bases also give compounds containing three molecules of the base to two of fluoride of silicon: paratoluidine, orthotoluidine, parachloraniline, diphenylamine, dimethylaniline, chinoline, and dimethylamine, the last giving also a compound having the formula  $((CH_3)_2NH)_4(SiF_4)_2$ . On the other hand, we have not succeeded in obtaining from ammonia a compound of the formula  $(NH_3)_3(SiF_4)_2$ .

We propose to call these substances silicotetrafluorides, a clumsy name, it is true, but one which will designate them with certainty, whereas all the simpler names, such as silicofluoride or fluosilicide, have been used for the fluosilicates at one time or another, and might therefore lead to confusion.

The remainder of the paper contains the detailed account of our experimental results, and at the end a discussion of our views in regard to the constitution of the silicotetrafluorides.

## PRODUCTS OF THE ACTION OF FLUORIDE OF SILICON ON ANILINE.

Trianiline Disilicotetrafluoride,  $(C_6H_5NH_2)_3(SiF_4)_2$ .— This substance was prepared by passing fluoride of silicon over aniline. The fluoride of silicon was made in the usual way, from calcic fluoride, sand, and sulphuric acid; but as we found that a glass flask after using it two or three times became perforated by the small quantities of hydrofluoric acid formed in the process, we replaced it by a thick

<sup>\*</sup> Chem. Centralblatt, 1862, p. 401.

glass bottle warmed in a water-bath, which lasted through a number of preparations. The delivery-tube should not dip below the surface of the aniline, as in that case there is danger that it will be stopped by the product; but if it is brought near the surface of the base, the action takes place so rapidly that very little of the fluoride of silicon is lost. A good deal of heat is given out during the reaction, and the aniline is converted into a loose white solid, which was washed with hot ligroine until free from aniline, and then its purification finished by two sublimations. The yield was essentially quantitative, 30 grams of aniline giving after treatment with fluoride of silicon for 24 hours 51 grams of product, instead of 52 grams, the amount which should be obtained for the formula \* (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>)<sub>5</sub>(SiF<sub>4</sub>)<sub>5</sub>. The same substance is formed when aniline fluosilicate is sublimed, and the preparation, the analysis of which is numbered I., was made in this way. It is to be observed that the substance analyzed by Laurent and Delbos was really prepared in this way, since by boiling their original product with alcohol they converted it into aniline fluosilicate, which was afterward reconverted into the silicotetrafluoride by sublimation. substance obtained by Knop by sublimation of his aniline fluosilicate was the trianiline disilicotetrafluoride.

The method of analysis used for all these substances consisted in neutralizing a weighed quantity of the substance dissolved in hot water in a platinum dish with a standard solution of sodic hydrate, using a solution of litmus as the indicator. The liquid was then heated to boiling, more of the sodic hydrate added, if the reaction had become acid, and evaporated to dryness on the water-bath, the residue treated with water, and the silicic dioxide filtered out. The filtrate, after neutralizing once more with the sodic hydrate, which is usually necessary when the organic base is one with an alkaline reaction, (NH, or (CH,),NH), is treated with a solution of zincic oxide in ammonic carbonate, evaporated once more to dryness on the waterbath, treated with water, and filtered; the precipitate is dissolved in strong nitric acid, evaporated to dryness, the residue after treatment with strong nitric acid extracted with water, and the silicic dioxide thus obtained added to that from the residue of the first evaporation, ignited, and weighed. The fluorine was usually calculated from the amount of the standard solution of sodic hydrate necessary for the neutralization of the hydrofluoric acid present, but it was also occa-



<sup>\*</sup> Laurent and Delbos found that 59.5 grm. of aniline absorbed 40.5 grm. of fluoride of silicon. Our formula requires 44.3 grm.

sionally determined direct in the filtrate from the zincic carbonate and silicate by evaporating to dryness in a platinum crucible, and, after removing any slight excess of sodic carbonate by converting it into acetate and washing with 80% alcohol, igniting and weighing as sodic fluoride.

- I. 0.2686 grm. of the substance gave 19.6 c.c. of nitrogen at a temperature of 23° and a pressure of 768 mm.
- II. 0.2982 grm. of substance gave 0.0751 grm. of silicic dioxide and 0.2105 grm. of sodic fluoride.
- III. 0.2842 grm. of substance gave 0.0717 grm. of silicic dioxide and 0.1968 grm. of sodic fluoride.
- IV. 0.3784 grm. of substance needed for neutralization 0.2480 grm. of sodic hydrate.

	Calculated for				
	$(C_6H_5NH_2)_3(SiF_4)_2$ .	I.	II.	III.	IV.
Nitrogen	8.62	8.31			
Silicon	11.50		11.75	11.77	
Fluorine	31.24		31.94	31.33	31.15

Several attempts to make a combustion of the substance have shown that great difficulties stand in the way of getting satisfactory results, and, as the determinations of nitrogen, silicon, and fluorine just given are sufficient to establish its formula beyond a doubt, we have not thought it worth while to devote to the study of the conditions of its combustion the time necessary to obtain an accurate result.

Properties.— The trianiline disilicotetrafluoride is a white semi-crystalline to amorphous solid, which sublimes in the neighborhood of 200° without melting. It is insoluble in ether (anhydrous), benzol, ligroine, chloroform, or carbonic disulphide. It is decomposed very slowly by boiling absolute alcohol without any deposition of silicic acid, and converted into aniline fluosilicate; we have not succeeded in bringing the other product of this reaction into a state fit for analysis; it is a thick liquid, probably a silicic ethylester. The action is more rapid with alcohol containing water. Water decomposes it at once with deposition of silicic acid, and the solution yields on evaporation aniline fluosilicate \* in beautiful white pearly scales. Its identity was determined by the following analysis.

0.7488 grm. of substance gave by precipitation with baric chloride 0.6372 grm. of baric fluosilicate.

<sup>\*</sup> W. Knop and W. Wolf, Chem. Centralblatt, 1862, p. 401.

	Calculated for		
	$(C_0H_8NH_8)_2SiF_6$ .		Found.
SiF <sub>6</sub>	43.04	•	43.30

To determine the proportions in which the substances act on each other when water is added to the trianiline disilicotetrafluoride, we have studied the reaction quantitatively with the following results.

1.3092 grm. of the substance were dissolved in water, and the silicic acid precipitated filtered out, ignited, and weighed, giving 0.1200 grm. of silicic dioxide. To the filtrate was added potassic chloride, and the potassic fluosilicate formed was dried at 100° and weighed, giving 0.7370 grm.

These numbers agree best with the following reaction: -

$$4 (C_6H_5NH_2)_3(SiF_4)_2 + 6 H_2O = 5 (C_6H_5NH_3)_2 SiF_6 + 2 C_6H_5NH_3F + 3 SiO_{2}$$

as is shown by comparing the amounts of the products which would be obtained from 100 grm. of trianiline disilicotetrafluoride according to it, and those which were actually obtained in the experiment just described.

	Calculated from		
	the Reaction.	Found.	
Silicic dioxide	9.25	9.17	
Aniline fluosilicate	84.70	84.41	

Two attempts were made also to determine the amount of aniline fluoride formed (both by titration and by conversion into calcic fluoride); but although these experiments proved the presence of a fluoride, they gave results which did not agree with each other or with the theory, the reason being without doubt that a portion of the aniline fluoride was converted into fluosilicate during the filtrations, which we had to carry on in a glass funnel.

The action of ammonia gas upon the trianiline disilicotetrafluoride was studied carefully, since we hoped that it might throw light on the constitution of this substance, and also that the corresponding ammonia compound  $(NH_3)_3(SiF_4)_3$  might be formed. Neither of these hopes has been realized, however, for upon passing ammonia gas over the trianiline disilicotetrafluoride the compound was decomposed with a strong evolution of heat, aniline was set free, and the product was the

<sup>\*</sup> As a matter of fact, it was one of the silicic acids which was precipitated; but as we do not know which one it was, we prefer to write it as silicic dioxide.

compound of ammonia and fluoride of silicon already described by J. Davy, as was proved by the following analyses, which also show that none of the desired substance  $(NH_3)_3(SiF_4)_2$  was formed; and as it was not obtained under these conditions, it is fair to suppose that it cannot exist. The substances for Analyses I. and II. were prepared by washing the aniline out of the crude product of the reaction with ligroine. The substance for Analysis III. was further purified by sublimation.

- 0.3414 grm. of the substance gave 0.1496 grm. of silicic dioxide and 0.4154 grm. of sodic fluoride.
- II. 0.4400 grm. gave 0.1937 grm. of silicic dioxide.
- III. 0.3770 grm. gave 0.1625 grm. of silicic dioxide.
- IV. 0.1920 grm. gave 0.0840 grm. of silicic dioxide.

	Calculated for	Found.			
	(NH <sub>3</sub> )4(SiF <sub>4</sub> )2.	I.	II.	ПI.	IV.
Silicon	20.29	20.44	20.55	20.12	20.41
Fluorine	55.07	<b>55.03</b>			

It was noticed during the purification of this substance that it sublimed at a much higher temperature than the trianiline disilicotetrafluoride. The reaction which takes place when trianiline disilicotetrafluoride is treated with ammonia gas is the following:

$$(C_6H_5NH_2)_3(SiF_4)_2 + 4NH_3 = (NH_3)_4(SiF_4)_2 + 3C_6H_5NH_2$$

as was proved by its quantitative investigation.

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2.8564 grm. of trianiline disilicotetrafluoride yielded after treatment with ammonia 1.6240 grm. of  $(NH_s)_4(SiF_4)_2$ .

Calculated Percentage according to the Reaction given above. Found. 
$$(NH_3)_4 (SiF_4)_2 \qquad \qquad 56.67 \qquad \qquad 56.85$$

When hydrochloric acid gas is passed over trianiline disilicotetrafluoride there is no action in the cold; but if the substance is gently warmed, complete decomposition sets in, aniline chloride sublimes along the tube in needles, and the hydrochloric acid contains fluoride of silicon, as was shown by passing it into water when a precipitate of silicic acid was formed.

The action of ethyliodide was also tried. At 100° there was no action, but at 150° a product was formed which contained neither fluorine nor silicon, fluoride of silicon being given off when the tube was opened. Under these circumstances, we did not think it worth

while to try to purify the residual substance for analysis. Ethylbromide acted in the same way, but with more difficulty. Strong sulphuric acid decomposes trianiline disilicotetrafluoride, giving off fluoride of silicon. The action of the other common reagents with this substance could not be studied, because it is decomposed by water or alcohol.

Dianiline Silicotetrafluoride, (C,H,NH,), (SiF,), - This substance was formed when aniline vapor was conducted into a receiver filled with fluoride of silicon, in the hope of preparing a compound containing a larger proportion of fluoride of silicon than that in the substance just described. The fact that, on the contrary, a body richer in aniline is formed, is probably to be accounted for by the high temperature at which the union of the two substances took place; and this view is confirmed by some experiments in which we heated the trianiline disilicotetrafluoride with one molecule of aniline to 150° in a sealed tube for about five hours: the product was a purplish mass, which gave results on analysis showing that a considerable quantity of aniline had been taken up, although not quite enough to convert the trianiline disilicotetrafluoride completely into the dianiline silicotetrafluoride. As the substance prepared directly from aniline and fluoride of silicon could not be purified on account of its slight stability, it was analyzed in the crude state with the following results, which are as accurate as could be expected under these circumstances.

- I. 0.3803 grm. of the substance gave 0.0826 grm. of silicic dioxide and 0.2255 grm. of sodic fluoride.
- II. 0.3032 grm. of the substance gave 0.0645 grm. of silicic dioxide and 0.1798 grm. of sodic fluoride.

	Calculated for	Found.	
	$(C_6H_5NH_2)_6(SiF_4)_2$	I.	11.
Silicon	$\boldsymbol{9.65}$	10.14	9.93
Fluorine	26.20	26.83	26.85

Properties.— It is a white powder which cannot be sublimed, as it decomposes with blackening when heated. With water it is decomposed and dissolved with deposition of silicic acid. It is possessed of but slight stability, as it gradually decomposes spontaneously even when kept in a corked tube at ordinary temperatures, the substance turning yellow and giving up aniline, which was extracted with ligroine, and recognized by its smell and its characteristic color with bleaching-powder, while the residue was pure trianiline disilicotetra-fluoride, as shown by the following analyses.

- 0.2370 grm. of the substance gave 0.0578 grm. of silicic dioxide and 0.1637 grm. of sodic fluoride.
- II. 0.1236 grm. of the substance gave 0.0841 grm. of sodic fluoride.

	Calculated for		Found.	
	$(C_0H_5NH_2)_3(SiF_4)_2$ .	(C <sub>6</sub> H <sub>8</sub> NH <sub>2</sub> ) <sub>4</sub> (SiF <sub>4</sub> ) <sub>3</sub> .	I.	II.
Silicon	11.50	9.65	11.39	
Fluorine	31.24	26.20	31.25	30.79

In view of this decomposition of the dianiline silicotetrafluoride into aniline and trianiline disilicotetrafluoride, and also of the formation of the dianiline silicotetrafluoride by heating aniline with trianiline disilicotetrafluoride, there seems no doubt that the real formula of this substance is  $(C_6H_5NH_2)_4(SiF_4)_2$ , that is, double the simplest formula determined by analysis, and that the reaction for its spontaneous decomposition is the following:

$$(C_6H_5NH_2)_4(SiF_4)_2 = C_6H_5NH_2 + (C_6H_5NH_2)_3(SiF_4)_2$$

ACTION OF FLUORIDE OF SILICON ON OTHER BASES.

Triorthotoluidine Disilicotetra fluoride,  $(C_7H_7NH_2)_3(SiF_4)_3$ . — This substance was prepared by passing fluoride of silicon into a solution of orthotoluidine in benzol, when a very heavy gelatinous precipitate was formed, which was purified by washing with benzol and three sublimations. It can be formed also by the methods given under the aniline compound, but precipitation from a benzol solution gives the result more easily, and furnishes a purer product. Its composition was determined by the following analyses.

- I. 0.2100 grm. of the substance gave 0.0476 grm. of silicic dioxide.
- II. 0.3530 grm. of the substance gave 0.2177 grm. of sodic fluoride.
- III. 0.2330 grm. of the substance gave 0.1440 grm. of sodic fluoride.
- IV. 0.2050 grm. of the substance gave 0.1266 grm. of sodic fluoride.

	Calculated for	Found.			
	(C7H7NH2)3(SiF4)3.	I.	II.	III.	IV.
Silicon	10.58	10.58			
Fluorine	28.73		27.90	27.97	27.94

Properties.—It is a white powder subliming without melting or decomposition, like the corresponding aniline compound. It dissolves in hot common alcohol, and the solution deposits on cooling orthotoluidine fluosilicate in fine needles.

Triparatoluidine Disilicotetrafluoride (C<sub>7</sub>H<sub>7</sub>NH<sub>2</sub>)<sub>3</sub>(SiF<sub>4</sub>)<sub>3</sub>. — This substance was made and purified like the corresponding ortho com-

pound, that is, by passing fluoride of silicon through a solution of paratoluidine in benzol, but even after four sublimations it had a distinct yellowish color; that the substance is essentially pure, however, in spite of this coloration, is shown by the following analyses.

I. 0.1928 grm. of the substance gave 0.0438 grm. of silicic dioxide. II. 0.1472 grm. of the substance gave 0.0922 grm. of sodic fluoride.

	Calculated for	Found.	
	(C7H7NH2)3(SiF4)2.	I.	II.
Silicon	10.58	10.60	
Fluorine	28.73		28.34

In properties it resembles the corresponding ortho compound, but is decidedly less stable, showing a strong tendency to turn yellow on standing, and the paratoluidine fluosilicate deposited, as the hot solution of the substance in alcohol cools, crystallizes in thick needles.

Trimonochloraniline Disilicotetrafluoride, (C<sub>6</sub>H<sub>4</sub>ClNH<sub>2</sub>)<sub>3</sub>(SiF<sub>4</sub>)<sub>2</sub>. — This substance was made by passing fluoride of silicon over parachloraniline, and was purified by sublimation. Its composition was determined by the following analysis.

0.4807 grm. of the substance gave 0.0990 grm. of silicic dioxide, and 0.2686 grm. of sodic fluoride.

	Calculated for	
	$(C_0H_4CinH_2)_3(8iP_4)_3$ .	Found.
Silicon	9.48	9.61
Fluorine	25.75	25.29

It resembles the corresponding aniline compound in its properties, and forms with hot alcohol a solution of the parachloraniline fluosilicate, which separates as the solution cools in beautiful long slender needles.

Parabromaniline forms a similar compound with fluoride of silicon, and gives with hot alcohol a solution depositing the parabromaniline fluosilicate in small pearly scales.

With symmetrical tribromaniline we could get no action, when we treated it with fluoride of silicon, the result of the experiment being negative, whether it was acted on alone in the solid state, or fused, or in solution in benzol. Symmetrical tribromaniline therefore does not combine with fluoride of silicon under the conditions which bring about the union with it of all the other bases studied.

Tridiphenylamine Disilicotetraftuoride, ((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH)<sub>5</sub>(SiF<sub>4</sub>)<sub>2</sub> — Solid pure diphenylamine is not acted on by fluoride of silicon; the

statement made in a preliminary notice of this work, that a compound was formed under these conditions was incorrect, the diphenylamine used for that first experiment being impure. If, however, fluoride of silicon is passed through a solution of diphenylamine in benzol, a white crystalline precipitate is deposited slowly, which was washed with benzol, dried at 100°, and analyzed with the following results.

- 0.4356 grm. of the substance gave 0.0695 grm. of silicic dioxide and 0.2141 grm. of sodic fluoride.
- II. 0.4192 grm. of the substance gave 0.1986 grm. of sodic fluoride.

	Calculated for	Fo	und.
	$((C_0H_5)_2NH)_3(SiP_4)_2$ .	I.	п.
Silicon	7.83	7.44	
Fluorine	21.26	22.23	21.43

Properties.—It forms thick white needles, which are decomposed by heat into fluoride of silicon and diphenylamine. When treated with water a precipitate of diphenylamine separates, and the filtrate contains fluosilicic acid. A quantitative study of the reaction gave the following results.

- 0.8135 grm. of the substance gave 0.5686 grm. of diphenylamine and 0.3040 grm. of potassic fluosilicate.
- II. 0.4934 grm. of the substance gave 0.3476 grm. of diphenylamine.

In the calculated percentages given below, it is assumed that all the diphenylamine is separated by the action of the water, and that four molecules of the compound will yield five of potassic fluosilicate, i. e. that the reaction with water is analogous to that of the corresponding aniline compound.

Calc	ulated.	Found.	
		I.	п.
Diphenylamine	70.91	69.89	70.44
Potassic fluosilicate	38.50	37.37	

If, as the numbers obtained seem to show, the reaction is similar to that of the trianiline disilicotetrafluoride with water, silicic acid should have been set free; but no trace of it could be discovered, the solution being free from any precipitate except the diphenylamine, and upon evaporation to dryness leaving no residue, while that silicic acid had not been carried down by the diphenylamine was shown by burning it, and also by dissolving it in benzol. In neither case did it leave a residue. We have not been able to find any explanation for this curious observation, or to account for the formation of fluosilicic acid

without the formation of silicic acid at the same time. That the soluble product was principally fluosilicic acid is proved by the fact that it gave a precipitate with potassic chloride.

Tridimethylaniline Disilicotetra fluoride, (C<sub>6</sub>H<sub>3</sub>N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>(SiF<sub>4</sub>)<sub>2</sub>—Fluoride of silicon has no action on dimethylaniline alone, but, if the gas is passed through a solution of dimethylaniline in benzol, a flocculent precipitate is formed, which is gradually converted into a gummy mass that crystallizes on standing. The crystals were purified by washing with benzol and ligroine, dried at 100°, and analyzed.

0.1066 grm. of the substance gave 0.0220 grm. of silicic dioxide and 0.0584 grm. of sodic fluoride.

	Calculated for	Found.
	(C <sub>0</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>3</sub> ) <sub>3</sub> (SiF <sub>4</sub> ) <sub>2</sub> .	
Silicon	9.81	9.63
Fluorine	26.62	24.77

The number for the fluorine is far from satisfactory, which is accounted for by the difficulty of purifying this decidedly unmanageable substance. It is, however, near enough to show that the substance can have no other composition than that assigned to it by us.

Properties. — It forms an indistinct crystalline mass, which is decomposed by heat, and gives no stable fluosilicate, when treated with alcohol.

Trichinoline Disilicotetra fluoride,  $(C_9H_7N)_3(SiF_4)_2$ . — Chinoline alone is not acted on by fluoride of silicon; but, if the gas is passed through a solution of chinoline in benzol, a gummy precipitate is formed at first, which becomes gradually converted into needle-shaped crystals. The product was purified by washing with benzol or ligroine, and dried at  $100^\circ$ . The same substance is obtained when chinoline fluosilicate is sublimed, and the analysis numbered II. is of a preparation made in this way.

I. 0.1634 grm. of the substance gave 0.0323 grm. of silicic dioxide. II. 0.0730 grm. of the substance gave 0.0404 grm. of sodic fluoride.

	Calculated for	Found.	
	$(C_9H_7N)_8(SiF_4)_9$	I.	II.
Silicon	9.41	9.23	
Fluorine	25.55		25.01

Properties. — It crystallizes in needles, and sublimes without melting, or decomposition. Although hot alcohol usually decomposes it,

as described below, on one occasion it dissolved it without decomposition, and this solution gave on cooling thick needles, which gave the following results on analysis.

0.0903 grm. of the substance gave 0.0176 grm. of silicic dioxide and 0.0506 grm. of sodic fluoride.

	Calculated for		
	$(C_9H_7N)_3(SiF_4)_2$ .	Found.	
Silicon	9.41	9.10	
Fluorine	25.55	25.38	

On addition of water the substance analyzed was decomposed with deposition of silicic acid. We have not succeeded, however, in repeating this experiment, as in all other cases the product from the action of hot alcohol has been chinoline fluosilicate, which crystallizes in long thick needles, as the solution cools, and gives a clear solution with water. Its composition was determined by the following analyses of the substance purified by two crystallizations.

0.1244 grm. of the substance gave 0.0200 grm. of silicic dioxide.
 0.2054 grm. of the substance gave 0.0325 grm. of silicic dioxide and 0.1254 grm. of sodic fluoride.

	Calculated for	Fo	und.
	(C <sub>9</sub> H <sub>7</sub> N) <sub>3</sub> H <sub>3</sub> SiP <sub>6</sub> .	I.	11.
Silicon	6.96	7.50	7.38
Fluorine	28.35		27.64

The trichinoline disilicotetrafluoride resembles the corresponding aniline compound closely in its properties.

Didimethylamine Silicotetrafluoride, ((CH<sub>3</sub>)<sub>2</sub>NH)<sub>4</sub>(SiF<sub>4</sub>)<sub>2</sub> — When dry dimethylamine (prepared according to Baeyer and Caro) was mixed with fluoride of silicon, a white powder was deposited, which was analyzed in the crude state, since it could not be purified because of its very slight stability.

0.2320 grm. of the substance gave 0.0740 grm. of silicic dioxide and 0.2038 grm. of sodic fluoride.

	Calculated for	
	((CH <sub>3</sub> ) <sub>2</sub> NH) <sub>4</sub> (SiF <sub>4</sub> ) <sub>2</sub> .	Found.
Silicon	14.43	14.89
Fluorine	39.17	39.75

Properties. — A white solid, which like the corresponding compound of aniline is very unstable, decomposing spontaneously at ordinary

temperatures into dimethylamine and the following compound, — a decomposition which is hastened by heat.

Tridimethylamine Disilicotetra fluoride, ((CH<sub>3</sub>)<sub>2</sub>NH)<sub>3</sub>(SiF<sub>4</sub>)<sub>2</sub>.—This substance was made by subliming the compound just described, when dimethylamine was given off as a secondary product. It was purified by a second sublimation, and its composition determined by the following analyses.

0.1871 grm. of the substance gave 0.0660 grm. of silicic dioxide.
 0.2800 grm. of the substance gave 0.0960 grm. of silicic dioxide and 0.2694 grm. of sodic fluoride.

	Calculated for	Fo	and
	((CH <sub>3</sub> ) <sub>2</sub> NH) <sub>3</sub> (SiF <sub>4</sub> ) <sub>2</sub> .	I.	II.
Silicon	16.33	16.46	16.00
Fluorine	44.31		43.53

Properties.—It is a white powder resembling the corresponding aniline compound in appearance and behavior when heated, although it sublimes at a higher temperature. It also differs from the aniline compound in being deliquescent.

Finally, we may add the following experiments, which gave products of so little promise that we did not attempt to analyze them, but which show that fluoride of silicon acts also on alkaloids, and on amides which can form salts.

Furfurine, when treated in benzol solution with fluoride of silicon, gave a gummy mass similar to that obtained from dimethylaniline, which however did not crystallize on standing.

Dry powdered urea was converted by fluoride of silicon into a pasty mass, which was decomposed with evolution of ammonia, when the attempt was made to sublime it. The sublimate contained fluorine and silicon, but we did not continue the study of it, as we had no guaranty that it was a homogeneous substance.

### CONSTITUTION OF THE SILICOTETRAFLUORIDES.

Although we have not succeeded in obtaining an absolute direct proof of the constitution of the substances described in this paper, we have been able to reduce the possible formulas that can be assigned to them to a very small number by the following course of reasoning. In the first place, we assume that all the substances described in this paper, which contain three molecules of the base combined with two of fluoride of silicon, have the same constitution, an assumption which is justified by the fact that they are all made

by the direct addition of fluoride of silicon to the base, and also by the strong resemblance in their properties, the differences observed being such as might well occur among substances belonging to the same class.

Upon considering, in general, the way in which the fluoride of silicon could attach itself to a base, we have been able to find only three probable methods, which we will proceed to discuss as applied to our compounds. (a.) By replacing the hydrogen of the amido group, forming a substance which would be at once an anilid and a fluosili-This method would seem at first sight the most probable, especially since A. Harden \* has found that chloride of silicon gives with aniline SiCl<sub>a</sub>(NHC<sub>a</sub>H<sub>a</sub>), and aniline chloride; but this mode of union is impossible, since both chinoline and dimethylaniline, which contain no hydrogen attached to their nitrogen, form compounds of (b.) By the action of the fluoride of silicon on the benzol ring, forming a substance analogous to pararosaniline fluosilicate. This hypothesis, which is improbable on account of the ease with which the substances are broken up by water, is rendered entirely inadmissible by the formation of the dimethylamine compound, which contains no ring. (c.) On the supposition that the fluoride of silicon combines with the base to form a sort of salt, this view is the only one compatible with our results, and its correctness is confirmed by the observation that all the substances tried formed salts with one exception, tribromaniline, and that this was the only one which did not form a silicotetrafluoride; further, the stability of the silicotetrafluorides keeps pace with the stability of the salts of the bases, those like aniline, the two toluidines, parachloraniline, chinoline, and dimethylamine, which form stable salts, giving silicotetrafluorides, which can be sublimed without decomposition, whereas diphenylamine and dimethylaniline gave compounds decomposed by heat. That the salts of diphenylamine are unstable, being decomposed by water, is well known, and although we have not been able to find any published statement about the salts of dimethylaniline that would imply they are unstable, our own work has furnished the proof that the fluosilicate at least is less stable than that of aniline, as only the products of the decomposition of the fluosilicate were obtained, when water was added to the tridimethylaniline disilicotetrafluoride.

We infer, then, from the arguments given above, that the nitrogen in the silicotetrafluorides is in the quinquivalent condition, and think it

<sup>\*</sup> J. Lond. Chem. Soc., 1887, i. 40. vol. xxiii. (n. s. xv.)

most probable that one of the two additional bonds is satisfied by silicon, the other by fluorine, and that the following graphic formula represents its constitution. It should be remembered, however, that this formula is only the most probable one, for, as already stated, we have been able to bring no absolute proof of its correctness.

If this formula is adopted, the formation of the silicotetrafluorides can be explained in the following way. In the first place one molecule of the fluoride of silicon acts upon one molecule of the base to give the group

$$_{C_{6}H_{5}}^{H_{2}}=N_{-F}^{-SiF_{2}}$$

and, although this mode of union seems strange at first sight, it is not without analogy, if we consider the close relationship of silicon and carbon, as then it is similar to the formation of ammonium salts by the action of methyliodide on a base, as shown by the following reactions:

$$\begin{split} & \overset{H_{2}}{\text{$C_{6}$H_{5}$N$H}_{2}$} + \overset{H_{2}}{\text{$C_{6}$H}_{5}$} - \overset{-}{N} \overset{\text{$CH$}_{8}$}{-1}; \\ & \overset{H_{2}}{\text{$C_{6}$H}_{5}$N$H}_{2} + \text{SiF}_{3}\text{F} = \overset{\text{$C_{6}$H}_{5}$}{\text{$C_{6}$H}_{5}$} - \overset{\text{$N$}}{N} \overset{\text{$-SiF$}_{8}}{-1}. \end{split}$$

Since the group

$$_{C_{\alpha}H_{5}}^{H_{2}}=N_{-F}^{-SiF_{3}}$$

is at once a fluoride and a substituted fluoride of silicon, an action next takes place similar to the formation of a fluosilicate from a fluoride and fluoride of silicon, thus:

$$\begin{array}{c} {\rm H_2} = N - {\rm Si} {\rm F_3} = {\rm H_2} = N - {\rm F} = {\rm F_2}; \\ {\rm C_6 H_5} - N - {\rm F} = {\rm F} - {\rm S_i} = {\rm F_2}; \\ {\rm K} - {\rm F} = {\rm F} - {\rm S_i} = {\rm F_2}. \end{array}$$

In this reaction the formation is assumed of the bivalent radical  $F_3^{\Pi}$ , which has been proved to exist in hydrofluoric acid by Mallet's determination  $^{*}$  of the vapor-density leading to the formula  $H_2F_3$ , and the assumption of the presence of which in fluosilicic acid explains its relation to silicic acid in the most satisfactory way. The substance

<sup>\*</sup> Am. Chem. J., iii. 189.

$$C_0H_2 = N_{-F_2} - S_i = F_2$$

next acts on another molecule of the base in the same way that the fluoride of silicon did originally, forming

$${}^{H_2}_{C_0H_5} = N \frac{H_2}{-F_2} = N \frac{H_2}{-F} = N \frac{-C_0H_5}{-F};$$

but it would seem that the acid nature of the silicon has been so weakened by the introduction of two aniline molecules, that the atom of fluorine left attached to the silicon cannot combine with the fluorine attached to the nitrogen, and therefore this latter is saturated by the more acid fluorine of a fluoride of silicon carrying only one aniline molecule, thus:

$$\begin{array}{l} c_{_{0}H_{_{5}}}=N \xrightarrow{\phantom{a}} S_{_{i}} = N \xrightarrow{\phantom$$

If then the two atoms of fluorine remaining attached simply to silicon are united, the formula given above is constructed. Our only reason for joining these last atoms of fluorine is that it makes the molecule more symmetrical, but it is also possible that they remain univalent.

Turning next to the compounds formed by the union of the base and fluoride of silicon in the proportion of two molecules of the former to one of the latter; as has been already argued, it is necessary to double the simplest formula which can be assigned to these substances, because they break up into the free base and the compound of three molecules of the base to two of fluoride of silicon, and also because they can be formed by a reaction the reverse of this decomposition. If, then, the formula discussed above is given to the trianiline disilicotetrafluoride, the formula of the dianiline silicotetrafluoride must be

$$C_{0}^{H_{2}} = N - F_{1} - S_{i}^{H_{2}} - N - C_{0}^{H_{5}} - S_{i}^{I} - F_{2}^{I} - S_{i}^{I} - F_{3}^{I} - N - C_{0}^{H_{5}}$$

and the very slight stability of the substance can be explained by the neutralization of the acid properties of the silicon and fluorine, already alluded to, by the introduction of so many molecules of base, which makes them hold the last molecule of the base with comparatively

little force. On the other hand, we have not been able to find any explanation for the stability of the compound derived from ammonia, as the only one we could think of — viz. that the ammonia being a stronger base than aniline would attach itself more firmly to the slightly acid molecule — is rendered inadmissible by the slight stability of the compound made from dimethylamine, a base nearly, if not quite, as strong as ammonia itself. It is possible that the ammonia compound has an entirely different constitution from the compounds of the organic bases, but we have no experimental material for testing the correctness of this hypothesis except Mixter's determination \* of the vapor density of this substance, which showed that it was dissociated into four volumes of ammonia and two of fluoride of silicon, and therefore that the simplest formula of the ammonia compound must be doubled, which would look as if it had a constitution similar to the organic compounds.

We may add that Harden † obtained by the action of chloride of silicon on pyridine, or chinoline compounds  $(C_5H_5N)_2SiCl_4$ , and  $(C_9H_7N)_2SiCl_4$ ; but as they give up chloride of silicon spontaneously, it is probable that they are not analogous in constitution to our substances.

The study of the action of fluoride of silicon on organic bases will be continued by one of us in this Laboratory.

<sup>\*</sup> Am. Chem. J., ii. 153.

<sup>†</sup> J. Lond. Chem. Soc., 1887, i. 40.

V.

### CATALOGUE OF ALL RECORDED METEORITES,

WITH A DESCRIPTION OF THE SPECIMENS IN THE HARVARD COLLEGE COLLECTION, INCLUDING THE CABINET OF THE LATE J. LAWRENCE SMITH.

By Oliver Whipple Huntington, Ph. D., Instructor in Mineralogy and Chemistry.

#### Presented June 15, 1887.

The nucleus of the collection of meteorites in the Mineralogical Museum of Harvard College was a small collection made by Professor Cooke, and representing altogether about fifty falls. In October, 1883, the well-known collection of J. Lawrence Smith was purchased for the College by subscription. Professor Smith, being anxious that the collection should be kept together, himself subscribed for the purchase. The following are the names of the subscribers:—

J. LAWRENCE SMITH.

JOSIAH P. COOKE.

ALEXANDER AGASSIZ.

ANNE WIGGLESWORTH.

H. H. HUNNEWELL.
MARTIN BRIMMER.
HENRY P. KIDDER.
GEORGE H. NORMAN.

With this addition the collection has become worthy of special notice, and is very rich in iron meteorites, of which about one hundred falls are represented, including several large individual specimens. The collection contains many fine examples of large cleavage crystals, which have been studied with great care, and are particularly described in this catalogue. It contains also numerous etched slabs, and in describing these attention is called to the character of the figures, and also to the variation of these figures, not only on different sections of the same meteorite, but frequently on different parts of the same section.

The collection of stones is not nearly so complete as that of the irons, and no attempt has been made to study their structure, or to

classify them lithologically, which has already been so admirably done by Tschermak and Brezina. In this catalogue no natural system of classification has been attempted, but the falls have been arranged chronologically, and, in the absence of any generally accepted system, this appears to be the most convenient order for reference.

In the arrangement of the catalogue, the left-hand column gives the dates of fall or find of all recorded meteorites, and in making out this list the catalogues of all the well-known museums were consulted; but where there were discrepancies the catalogue of the Vienna Collection was followed, in absence of positive evidence derived from original authorities. In the case of observed falls, the dates given must be very generally correct. It is quite different, however, with the "date of find," and we were constantly unable to reconcile the conflicting evidence on this point, which greatly interferes with the definiteness of a chronological arrangement.

The numbers in the second column, which we may call the catalogue numbers, designate the successive falls thus chronologically arranged. On the same line with the catalogue number is given the locality, the names by which the meteorite is commonly known being printed in small capitals; and these names alone appear in the index. In the third column are given the weights of the various specimens in the Harvard collection, and, at the right, a brief description of them. Before the description of the largest specimen under each fall, it is stated whether the specimen is an iron or a stone, without any attempt at a more exact specification, the object being merely to assist in the identification. In order to add authority to the catalogue, after the description of each specimen it is stated in brackets from whence it came into the possession of the College.

As it was found impossible to reconcile the statements of different catalogues in regard to pseudo-meteorites, no separate list of them has been made, but the opinions which we have formed in regard to the specimens in the Harvard collection are expressed in the context. It is impossible in this collection, as it must be in others, to establish beyond doubt the authenticity of some of the specimens, and discrepancies may readily arise on this account.

The specimens starred in the catalogue are duplicates intended for exchange, but will only be exchanged for masses of approximately similar weight and value.

The Harvard Cabinet also contains a great quantity of the Greenland iron, together with the associated rocks, which we hope to describe in detail in a subsequent paper.

The alphabetical index appended to this catalogue includes all the names by which the meteorites are commonly known, and refers both to the page and catalogue number.

Figures illustrating some of the most striking examples of crystalline structure have been grouped in five plates, and are referred to in the catalogue by numbers. On the plates, in connection with the number of the figure, is also given the number of the page on which the specimen is described.

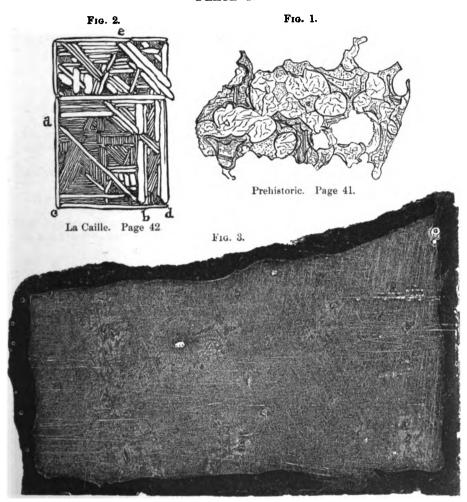
Although great care has been taken in the preparation of the catalogue, and many of the mistakes of previous catalogues have been corrected, yet the writer fears that many of the data which have been accepted on the best authority may be erroneous, and that this catalogue is by no means perfect. Even in regard to the circumstances of an observed fall, entire reliance can seldom be placed on the testimony of the original observers, who are often untrained, and overpowered by the startling phenomena; and there is frequently the difficulty of reconciling conflicting testimony. The connection between the fire-ball which attracted attention and the meteorite subsequently found is often only assumed, and not established.

The facts connected with the discovery of a meteorite are often more difficult to determine than those of an authentic fall. The only date which should be recognized is that of the publication in which the meteoric origin of the mass is first recognized; but after this is made known, it often appears that the specimen had been seen several years previously, and the discovery has been frequently antedated on the ground of such uncertain evidence. Again, it is often difficult to decide, especially in the case of meteoric irons, whether they really represent distinct falls. In some cases, pieces obviously of the same fall have become scattered over quite wide geographical areas, either as the result of successive explosions during the original flight of the meteorite, or else because distributed by human agency on account of some supposed value or sacred association. Moreover, the artificial value which rare meteoric specimens have acquired naturally inclines collectors to regard each new find as a distinct fall, and to enhance the value of the specimen by keeping it undivided. Such, and many other questions, which could not be settled with the limited means afforded even by so large a collection as that of Harvard College, have arisen in the preparation of this catalogue. Still, it is hoped that the work may be found of value in verifying and extending the history of these remarkable bodies.

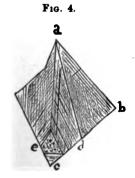
#### LIST OF ILLUSTRATIONS.

- Fig. 1. Prehistoric. Found on the altar of an Indian mound in Ohio, U. S. A.
- Fig. 2. La Caille. Etched face cut parallel to an assumed cube plane, and showing in section plates parallel to the regular dodecahedron octahedron and twin octahedron.
- Fig. 8. COAHULLA OR BUTCHER IRON. Printed directly from an etched slab of the meteorite, showing Neumann lines.
- Fig. 4. COAHULA OR BUTCHER IRON. Enlarged sketch, a cleavage crystal, a portion of a twin cube, with an octahedral modification.
- Fig. 5. COAHUILA OR BUTCHER IRON. Cleavage crystal showing how the Neumann lines can all be referred to a cube with twin members on all of the trigonal axes.
- Fig. 6. PUTNAM COUNTY. Etched face of a natural octahedron, showing Widmanstättian plates, and at the same time a granular structure.
- Fig. 7. CAREYFORT, DE KALE COUNTY. Showing the etched figures on a surface cut parallel to a natural octahedral face.
- Fig. 8. Braunau. Showing twinning lines as they appear on a natural cube face.
- Fig. 9. CRANBERRY PLAINS. Two faces of a natural octahedron, showing on one side bent plates, and on the other only a mottled surface.
- Fig. 10. Knoxville, Tazewell County. An etched face, showing very fine octahedral crystallization.
- Fig. 11. COOPERTOWN, ROBERTSON COUNTY. Showing etched figures on an octahedral face, and a face cut at right angles. The plates lettered a are cubic, those lettered b dodecahedral, and the rest octahedral.
- Fig. 12. RUSSEL GULCH. Printed directly from an etched slab, showing bent Widmanstättian plates.
- Fig. 18. FRANKFORT, FRANKLIN COUNTY. Large cleavage octabedron.
- Fig. 14. BARRANCA BIANCA. Etched face, showing very striking figures.
- Fig. 15. BUTLER, BATES COUNTY. Shows an etched face with Widmanstättian figures, extending to the finest Neumann lines. The small figure at the left, shows one face of a very perfect cleavage octahedron with octahedral and dodecahedral markings.
- Fig. 16. MIGA FROM CHANDLER'S HOLLOW, DELAWARE, with depositions of magnetite along the planes of crystalline growth, showing the formation of figures similar to the Widmanstättian, by the exclusion of foreign material in the process of crystallization.

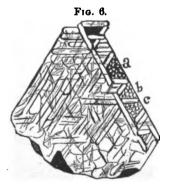
### PLATE I.



Coahuila (Butcher Iron). Page 59.



Coahuila (Butcher Iron). Page 59.



Putnam County. Page 61.

### PLATE II.

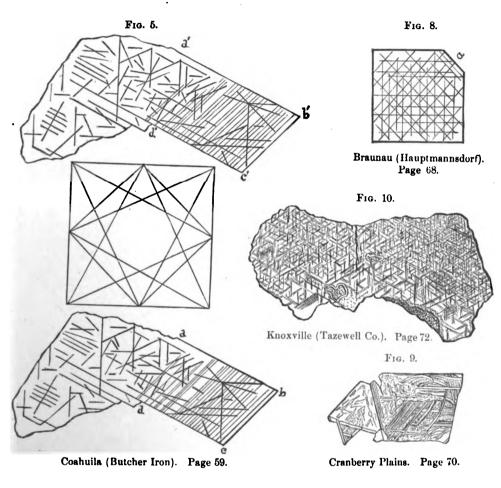
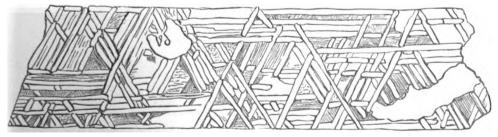
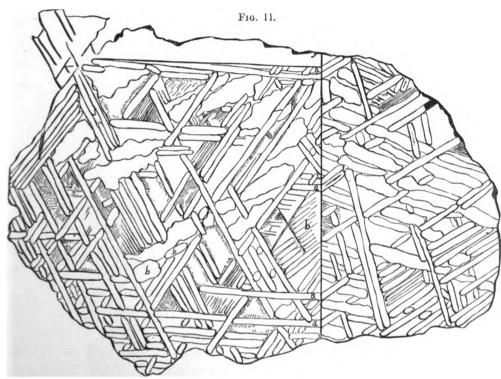


Fig. 7.



Careyfort (De Kalb Co.) Page 64.

# PLATE III.



Coopertown, Robertson County. Page 79.

F1G. 12.



Russel Gulch. Page 83.

Fig. 14.



Barranca Blanca. Page 86.

# PLATE IV.

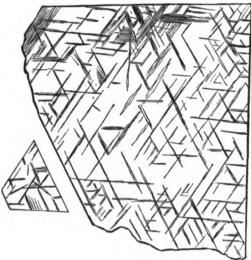
Fig. 13.



Franklin County. Page 86.

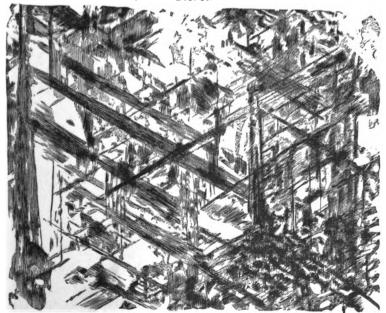
# PLATE V.

Fig. 15.



Butler (Bates Co.). Page 92.

Fig. 16.



Mica from Chandler's Hollow (Delaware). Page 40.

Date of Fall or Find,	No.	Weight in Grams.	Description.
Prehistoric.	1	187	Anderson, Little Miami Valley, Ohio, U. S. A.  Found on the altar of Mound No. 4 of the Turner Group of earthworks in Little Miami Valley.  The greater portion of the original mass. One polished face. Structure closely resembling the Pallas iron.  [From the Peabody Museum.]  * Full-sized slab, polished and etched, differing from the Pallas and Atacama meteorites in showing, occasionally, well-marked Widmanstattian plates, crossing completely the iron portions, without regard to the more minutely crystallized parts, as shown in the
Prehistoric.	2		ANDERSON, LITTLE MIAMI VALLEY, Ohio, U. S. A.  Found on the altar of Mound No. 3 of the Turner Group.  Mass of iron, with one face cut and etched, showing figures closely resembling those of the Coahuila irons.  [From the Peabody Museum.]
Fell 1164. Found 1751.	3	5	STEINBACH, Saxony.  Network of iron, enclosing olivine grains. One face polished and etched, the iron showing well-marked Widmanstattian figures, about like Jewell Hill or Obernkirchen. [Smith Collection. From W. Nevile.]
Fell 1164? Found 1847.	3	225.3 38 13	RITTERSGRUN, Erzgebirge, Saxony.  Slab polished and etched on all but one edge, where it shows the crust. Same network of iron enclosing grains of olivine and magnetite. [Purchased from the Liebener Collection.]  * Similar to the previous polished slab. [Smith Collection. From James R. Gregory.]  * Only one face polished, the rest crust. [Smith Collection.]

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1164? Found 1861,	3	61 60 22	Breitenbach, Platten, Bohemia.  Four polished faces cut at right angles to each other, and the rest crust. [Smith Collection. From Wöhler.]  Like the previous specimen. [Smith Collection. From Wöhler.]  Ragged specimen, appearing rougher than the specimens of Steinbach and Rittersgrün, and showing beautiful glassy crystals of olivine, highly modified. All the specimens of this group have effusions of chloride of iron. [Smith Collection. From Wöhler.]
Fell 1400? Recognized 1811.	4	147 23.2	Elbogen, Bohemia.  Iron. One large polished surface, the rest showing crust. [Smith Collection.]  Beautifully etched slab, showing well marked Widmanstättian figures. [Smith Collection.]
Fell 1492. Nov. 16, 124 p. m.	5	22 8.4	Ensisheim, Elsass, Germany.  Stone. One polished surface, showing a mass of iron in one part, and iron grains distributed through the rest.  [Smith Collection. From Wöhler.]  Irregular fragment. [Smith Collection. From Wöhler.]
Known in 1600? Recognized 1828.	6	804.2	LA CAILLE, near Grasse, Alpes Maritimes, France.  For about two centuries it was in front of the church of La Caille, and was used as a seat. Its meteoric origin was recognized by Brard in 1828.  Highly crystalline iron. Shows three natural octahedral faces, and one dodecahedral face an inch in dismeter, which is exactly at 145° with an adjacent octahedral face as shown by an application goniometer. This face, being a single plate, shows no figures when etched, but only a mottled appearance. Fig. 2 shows of original size an etched face of this specimen, cut parallel to an assumed cube face. There is also another etched face cut at right angles to the one in the figure, so that the direction of the plates may be observed. In

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Date of Fall or Find.	No.	Weight in Grams.	Description.
			Fig. 2 octahedral plates appear in section running parallel to $ac$ and $cd$ , while those in the direction $ab$ are parallel to the dodecahedron, and those in the direction $ce$ , making an angle of 66° 19' with $cd$ , are plates of the twin octahedron. [Smith Collection.]
Fell 1668. June.	7		Vago, near Caldiero, Verona, Italy.
Fell 1715. April 11, 4 p. m.	8		SCHELLIN, Garz, near Stargard, Pomerania, Prussia.
Fell 1723. June 22.	9		PLOSCHKOWITZ, REICHSTADT, Bohemia.
Fell about 1730.	10		Ogi, Kiusiu, Japan.
Found 1749.	11	172 9 54.5	MEDWEDEWA, KRASNOJARSK, Siberia.  (The Pallas iron.) Ragged mass, with one surface cut and polished, showing network of iron enclosing olivine grains. [Purchased from Louis Saemann, Paris.]  * Ragged specimen, most of the olivine having fallen out. [Smith Collection. From Louis Saemann.]  * Ragged specimen, like the above. [Purchased from Louis Saemann.]
Fell 1751. May 26, 6 p. m.	12	6.3	AGRAM, HRASCHINA, Croatia. First iron seen to fall.  Thin plate, polished on one side and etched on the other, showing fine Widmanstättian figures. [Smith Collection.]
Fell 1753. July 8, 8 r. m.	13	14.8	Krawin, Tabor, near Plan and Strkow, Bohemia. Gray stone, full of rusty iron grains. Three cut faces at right augles, the rest showing dull, black crust. [Smith Collection.]
Fell 1753. Sept. 7, 1 p. m.	14		LUPONNAS, Ain, France.
Known 1763.	15	22.8	SIRATIK, SENEGAL, West Africa.  Iron. Etched surface appears mottled, with occasional fine lines, but on being magnified the entire surface shows minute crystallization. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1766. Middle of July, 5 r. m.	16		ALBARETO, MODENA, Italy.
Fell 1768. Sept. 13, 44 P. M.	17		Luce (Maine), Sarthe, France.
Fell 1768. Nov. 20, 4 p. m.	18	9	MAUERKIRCHEN, Bavaria, now Austria. Stone. Light gray, with fine iron grains. Irregular fragment, showing dull black crust. [Smith Collection.]
Fell 1778. Nov. 17, 12 a. m.	19		SENA, SIGENA, Aragon, Spain.
Found 1783.	20	149	CAMPO DEL CIELO, OTUMPA, TUCUMAN, Argentine Republic, South America.  Iron. Irregular slab, with one face polished and etched. The figures brought out by the acid are peculiar, consisting of unusually broad and somewhat indefinite plates, most of which are cracked into irregular polygonal masses, while others are compact and exhibit beautiful Neumann lines. [Purchased from Ward and Howell.]  • Irregular mass with one face polished and etched, but showing no fig-
Found 1784.	21		tires. [Smith Collection.] SIERRA BLANCA, DURANGO, Mexico.
Found 1784.	22	248	IXTLAHUACA, TOLUCA, Mexico.  Iron. Specimen shows crust, also three faces cut at right angles and etched, showing well-marked Widmanstattian figures. [Purchased from Ward and Howell.]
Found 1784.	22	<b>14,74</b> 0	XIQUIPILCO, TOLUCA, Mexico.  A complete individual, covered with a smooth crust, which flakes off in scales
		18,869	if exposed to the air. [Smith Collection.]  Large mass with crust, and one polished face, showing large nodules of
; ;		786	troilite. [Smith Collection.]  Very thin polished slab, full size, showing sections of unusually large
H		88	modules of troilite. [Smith Collection.]  * Slab, etched, showing very good Widmanstättian figures, also crust. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1784.	23	14.3	Bembdego, Bahia, Brazil.  Iron. One face etched, showing imperfect Widmanstattian figures. [Smith Collection.]
Found 1784.	24	8.5	HACIENDA DE CONCEPCION, CHIHUA- HUA, Mexico. Iron. Irregular piece. [Smith Col- lection. Gift of Dr. H. B. Butcher.]
Fell 1785.	25		WITTMESS, EICHSTÄDT, Bavaria.
Fell 1787. Oct. 13, 8 p. m.	26		KHARKOV, Bobrik, Russia.
Fell 1790. July 24, 9 p. m.	27	10	BARBOTAN, Landes, France. Stone. Gray groundmass, partly breecia and partly rounded grains. Polished face, showing grains of iron thickly distributed through the mass. [Smith Collection.]
	1	2.3	* Some small bits. [Smith Collection.]
Found 1792.	28	148.2 138	ZACATECAS, Mexico.  Iron. One face etched, showing figures little better than cast-iron. [Smith Collection.]  Similar to previous specimen. Shows octahedral structure on surface of fracture. [Smith Collection.]
Found 1793.	29	110.5	CAPE OF GOOD HOPE, South Africa. Thin slab of iron. Etched, but showing no figures. [From the collection of Baumhauer and Stürtz.]
Fell 1794. June 16, 7 p. m.	30	5	SIENA, Tuscany, Italy. Stone, gray, breccia-like, with grains of iron scattered through the mass. Specimen shows dull brown crust, and one polished face. [Smith Collection.]
Fell 1795. Dec. 13, 24 r. m.	81	65 1.5	Wold Cottage, Thwing, Yorkshire, England. Stone, with dull brown crust. Two polished surfaces at right angles show grains of iron very unequally distributed through the mass. The specimen is intersected by several cracks filled in with crust. [Smith Collection.]  * Small bits. [Smith Collection.]
Fell 1797.	32		BJELAJA ZERKOW, Ukraine, Kiew, Russia.

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1798. March 8-12, 6 p. m.	33	6.5	SALLES, Villefranche, Rhône, France. Stone, light gray, compact. One polished face showing grains of iron scattered through it. Brown crust. [Smith Collection.]
Fell 1798. Dec. 18, 8 p. m.	34		KRAHUT, BENARES, India.
About 1800.	35	187 118.5 165 78 2.5 2.0	IMILAC, ATACAMA, Bolivia, South America.  Iron network enclosing olivine grains, like the Pallas iron.  Slab, polished and etched, the iron in some parts showing well-marked typical Widmanstattian figures.  Slab, polished and etched like the previous specimen.  Irregular mass, considerably weathered on the exterior.  Like the previous specimen, only a little more ragged from some of the olivine grains having fallen out.  Ragged bits of the iron.
Found 1802.	36	252	ALBACHER MÜHLE, BITBURG, Rhenish Prussia.  Iron. Porous mass looking like an iron slag, owing to its having been passed through a furnace at Trèves. The specimen has two polished faces cut at right angles, but shows no figures when etched. In one part shows a distinct black crust. [Smith Collection. From James R. Gregory.]
Fell 1803. April 26, 1 p. m.	37	90 76	L'AIGLE, Normandie, Orne, France. Stone, gray, compact, with rusty iron grains. Shows dull brown crust. [Smith Collection.] * Fragment without crust. [Purchased from Ward and Howell.]
Fell 1803. Oct. 8, 10 a. m.	38	127	SAURETTE, APT. VAUCLUSE, France. Stone. Large polished slab, with rusty grains of iron thickly distributed through the mass, giving it a mottled brown color. [Smith Collection.]
Fell 1803. Dec. 18, 10} a. m.	<b>3</b> 9		SAINT NICHOLAS, MASSING, Bavaria.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Known 1804.	40	37	CHARCAS, SAN LUIS POTOSI, Mexico.  Iron. Thin slab, showing crust and three polished faces. One etched face shows typical Widmanstattian figures.  [This specimen was presented to Prof.
		14	J. Lawrence Smith by the Paris Museum.]  A piece showing crust, also three polished faces. This specimen bears the same stamped number of J. L. Smith's Catalogue, but shows no Widmanstättian figures, and is more probably a specimen of one of the Coahuila irons.
Known 1804.	41		Misteca, Oaxaca, Mexico.
Found 1804.	42	<b>34</b>	RANCHO DE LA PILA, DURANGO, Mexico. Iron. Thin slab, highly polished on one side; other side etched, showing typical Widmanstättian figures. Crust on edges. [Smith Collection.]
Found 1804.	43		Darmstådt, Hesse.
Fell 1804.	44		High Possil, Glasgow, Scotland.
Fell 1804. Nov. 24.	45		HACIENDA DE BOCAS, SAN LUIS POTOSI, Mexico.
Fell 1805. April 6, 5 p. m.	46		DORONINSK, Irkutsk, Siberia.
Fell 1805. June, Day.	47		Constantinople, Turkey.
Fell 1805.	48		Asco, Corsica.
Fell 1806. Mar. 15, 5 p. m.	49	6.5	ALAIS, Gard, France. Stone. Small fragments of dark brown earthy meteorite. [Smith Collection.]  Also some powder. [Exchanged with C. U. Shepard from the cabinet of Vauquelin.]
Fell 1807. Mar. 25, p. m.	50	7	TIMOSCHIN, SMOLENSK, Russia. Stone. Light gray with rusty iron grains, and black crust. [Smith Collection.]

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1807. Dec. 14, 6.80 a.m.	51		WESTON, FAIRFIELD Co., Connecticut, U. S. A.
		135.5	Stone. Looking something like a mass of old mortar. Gray with rounded grains, like a fine conglomerate, with specks of iron scattered through it, and showing a dull black crust. [Smith Collection.]
		20.5	<ul> <li>Irregular fragment, showing crust.</li> <li>[Smith Collection.]</li> </ul>
		15.5	* Irregular fragment, showing crust. [Smith Collection.]
		17	* Same, without crust. [Smith Collection.]
		16	* Same, without crust. [Old Collection.]
		11	* Same, without crust. [Old Collection.]
		6	* Same, without crust. [Old Collection.]
		2	* Same, without crust. [Smith Collection.]
Fell 1808.	52		MORADABAD, Northwest Provinces, India.
Found 1808.	53	1,737	CROSS TIMBERS, RED RIVER, Texas.  Iron. Slab, from the "Gibbs Meteorite" of Yale College. Etched, showing typical Widmanstattian figures.  [Presented by Dr. W. Gibbs from the
		22	cabinet of his father.] Fragment, with one face polished. [Smith Collection.]
Fell 1808. April 19, 12 m.	54	.5	Borgo San Donino, Cusignano, Noceto, Parma, Italy. Stone. Light gray with dull black crust. [Smith Collection.]
Fell 1808. May 22, 6 a. n.	55	183.5	STANNERN, IGLAU, Moravia.  Stone. A complete individual coated with a black vitreous crust, covered with a curious veining, as if the palm of the hand had been pressed upon it
		80.5	and removed when the coating was semi-fluid. [Smith Collection.]  Fragment of gray and white stone nearly covered with crust, but only

Date of Fall or Find.	No.	Weight in Grams.	Description.
		11	part of the crust exhibiting the veined character just mentioned. [Smith Collection.]  * Fragment without crust. [Purchased from the Liebener Collection.]
Fell 1808. Sept. 8, 34 p. m.	56	6.5	Lissa, Bunzlau, Bohemia.  Stone. Gray, with very little iron, and smooth dull black crust. [Smith
		.5 .5	Collection.] Fragment, showing crust. [Smith Collection.]
		.0	Fragment, showing crust. [Smith Collection.]
Found 1809.	57		Kikino, Viasma, Smolensk, Russia.
Found 1810.	58	85	ROKIČKY, BRAHIN, MINSK, Russia.  Iron. Ragged end, with one face polished, and etched, but showing only Neumann lines. [Smith Collection.]
Found 1810.	59		Santa Rosa, Tunja, New Granada, South America.
Found 1810.	60		CHARTRES, Eure et Loire, France.
Found 1810.	61		RASGATÀ, TOCAVITA, New Granada, South America.
í		4 or 5	Iron. Thin slab, mounted in cement. Polished face shows well-marked Widmanstattian figures. [In exchange from S. C. H. Bailey.]
Fell 1810. August, Noon.	62	7	Mooresfort, Tipperary, Ireland.  Stone. Dark gray, with smooth black crust. One polished face shows iron grains thickly distributed through the mass. [Smith Collection. From W. Nevile.]
Fell 1810. Nov. 23, 11 p. m.	68	80.5 4 1	CHARSONVILLE, near Orleans, Loiret, France.  Stone. Dark gray, full of rusty iron particles. Fragment, without crust. [Smith Collection.]  Fragments, without crust. [Smith Collection.]

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Date of Fall or Find.	No.	Weight in Grams,	Description.
Fell 1811. March 12, 11 a. m.	64	5	KULESCHOVKA, POLTAVA, Russia.  Stone. Light gray fragment, divided by a vein of black crust. [Smith Collection.]
Fell 1811. July 8, 8 p. m.	65	2 1 .5}	Berlanguillas, Burgos, Castile, Spain.  Stone. Gray, with iron grains. Irregular fragment, without crust. [Smith Collection. From C. U. Shepard.]  * Fragments like the previous specimen. [Smith Collection.]
Fell 1812. Aprii 10, 1} p. m.	66	·	Toulouse, Haute Garonne, France.
Fell 1812. April 15, 4 p. m.	67	1.5	ERXLEBEN, MAGDEBURG, Prussia.  Stone. Irregular fragment of gray stony meteorite, with polished face showing considerable amount of iron.  [Smith Collection.]
Fell 1812. August 5, 2 a. m.	68	<b>43</b> .5	CHANTONNAY, Vendée, France.  Stone. Irregular fragment, nearly black, with black crust. Shows flakes and veins of iron through the mass.  [Smith Collection.]
Fell 1813. Sept. 10, 6 a.m.	69	50	LIMERICE, ADARE, Ireland.  Stone. Dark gray, with smooth dull brown crust. Polished surface, showing iron grains thickly distributed.  [Smith Collection.]
Fell 1813. Dec. 13, Day.	70		LUOTOLAES, Wiborg, Finnland.
Found 1814.	71	50	LENARTÓ, Sáros, Hungary.  Iron. Square slab, etched on all sides, showing typical Widmanstattian figures. [Smith Collection. From C. U. Shepard.]
		40.5	Etched slab, showing crust on edges, also octahedral cleavage. [Smith Collection.]  * Irregular mass. [Purchased from Liebener Collection.]
Found 1814.	72		GURRAM KONDA, Madras, India.

F		Walls	
Date of Fall or Find.	No.	Weight in Grams,	Description.
Fell 1814. Sept. 15, m.	78	2.5	ALEXEJEWKA, BACHMUT, Ekaterinoslav, Russia. Stone. Very light gray. Fragment, with two polished faces showing iron grains.
Fell 1814. Sopt. 5, m.	74	9	AGEN, Lot-et-Garonne, France. Stone. Gray, with rusty grains of iron through the mass. [Smith Collection]
		4.5	lection.]  * Like the previous one, but showing
		1.5	erust. [Smith Collection.]  * Fragment of gray stone with dull brown crust, and showing a vein of crust through the mass. Not rusty.  [Smith Collection.]
Fell 1815. Feb. 18, m.	75	22	DURALA, Umbala, Delhi, India. Stone. Light gray, with darker grains, and considerable iron. Shows black porous crust. [Smith Collection]
		20	tion.]  * Slab, with two polished faces, and crust on the edge. [Smith Collection.]
Fell 1815. Oct. 3, 8 a. m.	76	8.2	CHASSIGNY, Haute-Marne, France. Stone. Small fragments in a bottle, yellowish white color, with dark brown crust. [Smith Collection. From Daubrée.]
Found 1818.	77	444	CAMBRIA, LOCKPORT, New York, U. S. A. Iron. Mass with one polished face, the rest crust, showing imperfect octa- hedral structure. Shows on the face large inclusions of troilite. [Smith Col-
		168.5	ection.]  * Full-sized slab, from the above specimen, showing troilite nodule.  Also shows Widmanstättian figures on
		79.5	the polished surface.  Similar to previous slab, only with one end cut off. Face, polished and etched, shows most beautiful Widmanstättian figures.
Found 1818.	78	795	BABB'S MILL, GREEN Co., Tennessee, U.S.A. Iron. Mass, with deeply pitted crust. One end cut off and polished. On

Date of Fall or Find.	No.	Weight in Grams.	Description,
		115 55	being etched the surface only darkens, but shows no figures whatever. [Smith Collection.]  * Rough mass, cut from previous specimen, covered with crust, except on two polished faces cut at right angles.  * Thin, polished slab, cut from the
		25	same specimen as the previous one.  * Same as the above specimen.
Fell 1818. April 10.	79		ZABORZIKA, VOLHYNIA, Russia.
Fell 1818. June.	80	19	SERES, Macedonian Turkey.  Stone. Black and gray, containing grains of iron, and showing a curious porous black crust. [Smith Collection.]
Fell 1818. August 10.	81	<b>4</b> .5	SLOBODKA, SMOLENSK, Russia. Stone. Very light colored, and scattered through with fine iron grains. [Smith Collection.] Like the previous one, only in addition showing a dull dark brown crust.
Found before 1819.	82	1 .	[Smith Collection.]  Burlington, Otsego Co., New York, U. S. A.
Fell 1819. June 18, 6 a. m.	88	.8 .8 .3	SAINTONGE, JONZAC, France. Stone. Three small irregular fragments.
Fell 1819. Oct. 18, 8 a. m.	84	1}	Politz, near Gera, Reuss, Germany.  Stone. Irregular fragments of a dark gray color with white specks, also dull black crust. [Smith Collection.]  * Numerous smaller fragments like the above. [Smith Collection.]
Found 1820.	85		GUILFORD COUNTY, North Carolina, U.S.A.
Fell 1820. July 12, 51 p. m.	86	5	LASDANY, LIXNA, Witebsk, Russia.  Stone. Dark gray. One face polished, showing considerable iron, and cracks in every direction filled with crust, giving it a breccia-like appearance. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1821. June 15, 84 p. m.	87	71	JUVINAS, Ardèche, France.  Stone. Gray, almost no iron, but shows black vitreous crust. [Smith Collection. From J. G. Gregory.]
		1.2	* Fragment, showing crust. [In exchange from C. U. Shepard.]
Fell 1822. June 8, 81 p. m.	88		Angers, Maine-et-Loire, France.
Fell 1822. August 7.	89		KADONAH, AGRA, India.
Fell 1822. Sept. 18, 7 a. m.	90		LA BAFFE, ÉPINAL, Vosges, France.
Fell 1822. . Nov. 30, 6 p. m.	91	81.5	ALLAHABAD, FUTTEHFUR, India. Stone. Very light colored, nearly white, with smooth brown crust. One face polished, showing considerable iron, and numerous cracks filled with iron and the fused crust. Also shows partially formed crust on surface of
		24	fracture. [Smith Collection.]  * Showing same features as previous specimen, but with two polished faces. [Smith Collection.]
Fell 1822–23.	92		Umballa, Delhi, India.
Fell 1823. Aug. 7, 41 p. m.	98	8	Nobleboro, Lincoln Co., Maine, U.S.A. Stone. Light gray, with darker grains. Very little iron. [Old Collection.]
Fell 1823.	94		Botschetschki, Kursk, Russia.
Fell 1824. Jan. 15, 84 p. m.	95	41	RENAZZO, FERRARA, Italy. Stone. Black mass containing white grains, looking like a porphyry. Black
		25	porous crust. [Smith Collection.]  * Similar to previous specimen, showing crust. [Liebener Collection. Pur-
		9.5	chased.]  * Without crust. [Liebener Collection.  Purchased.]
Fell 1824.	96		Tounkin, Irkutsk, Siberia.
Fell 1824. Oct. 14, 8 a. m.	97		Praskoles, Zebrak, Bohemia.

Date of Fall or Find.	No.		Description.
	_	Grams,	
Fell 1825. Feb. 10, 12 A. M.	98	117	NANJEMOY, Charles Co., Maryland, U.S. A Stone. Light gray, with darker grains and considerable iron. One end shows a smooth black crust, the other a thick porous black crust. [Gift of Dr.
		4.5	W. Gibbs, from cabinet of his father.]  * Fragment showing crust. [Smith]
		1.3	Collection.]  * Fragment without crust. [Smith Collection.]  * Also numerous smaller fragments.
Fell 1825. Sept. 14, 10½ a. m.	99	37.5	Honolulu, Oahu, Sandwich Islands. Stone. Nearly covered with dark brown crust, deeply pitted. On frac- ture very light gray color, but inter- sected by a network of cracks filled with crust. Grains of iron scattered through the mass. [Smith Collection.]
Found 1826.	100		NAUHRIM, Frankfurt, Hessen.
Found 1826.	101		GALAPIAN, AGEN, Lot-et-Garonne, France.
Fell 1826. May 19?	102	135 63.5	Mordvinovka, Pavlograd, Ekaterinoslav, Russia. Stone. Slab with two polished faces and thin black crust on edges. Light gray, with darker grains surrounded by iron. Chloride of iron appearing on the surface.  * Block, with two polished faces, and crust. [Smith Collection.]
Found 1827.	108		NEWSTEAD, ROXBURGHSHIRE, Scotland.
Fell 1827. Feb. 16, 8 p. m.	10 <del>4</del>		Мноw, Azamgarh District, India.
Fell 1827. May 9, 4 s. m.	105	1,200	DRAKE CREEK, NASHVILLE, Tennessee, U. S. A. Stone. Light gray. Sprinkled through with iron grains. Crack through the mass filled with crust. Fragment largely covered with dull brown crust, deeply pitted. [Smith Collection.]
		120.5	* Fragment, showing crust. [Smith Collection.]
		105	* Fragment, showing crust. [Purchased from Ward and Howell.]

	,		
Date of Fall or Find.	No.	Weight in Grams.	Description.
		50 2 2 2 2	* Fragment, showing crust. [Smith Collection.]  * Other small fragments, without crust.
Fell 1827. Oct. 5, 94 A. M.	106		Jasly, Bialystok, Russia.
Known in 1827.	107	820	SANCHA ESTATE, SANTA ROSA, SALTIL- LO, COAHUILA, Mexico. Iron. Sawed slab. Full section. [From Smithsonian Institute, in exchange.] Slab, broken, showing perfect cubic cleavage like galena. Distinguished from the other Coahuila irons by the cleavage. [In exchange from S. C. H.
		3.5 3.5 2.5 1.5	Bailey.] Thin etched slab, showing Neumann lines. [Smith Collection.] Irregular fragments. [Smith Collection.]
Fell 1828. June 4, 8} A. M.	108	3 2	RICHMOND, Henrico Co., Virginia, U. S. A. Stone. Black and white grains. [Smith Collection. From C. U. Shepard.]  * Gravel.
Found 1829.	109	49	BOHUMILITZ, PRACHIN, Bohemia. Iron. Etched slab, showing broad, well-defined Widmanstättian figures. Crust on edges. [Smith Collection.]
Fell 1829. May 8, 3½ p. m.	110	68.5 1 .5	FORSYTH, Monroe Co., Georgia, U. S. A. Stone. Light gray, with little iron. [Smith Collection.]  * Small irregular fragments. [Smith Collection.]
Fell 1829. Aug. 14, 11; p. m.	111		DEAL, near Long Branch, New Jersey, U. S. A.
Fell 1829. Sept. 9, 2 p. m.	112		Krasnoj-Ugol, Räsan, Russia.
Fell 1830. May 17.	118		PERTH, Scotland.
Fell 1831. July 18.	114	112.5	VOUILLE, Poitiers, Vienne, France. Stone. Gray, compact, sprinkled with iron grains. Dull black crust. [Smith Collection.]

Date of Fall or Find.	No.	Weight	Description
Deser of Pall OF PIRG.	110.	Grams,	Description.
Fell 1831. Sept. 9, 31 p. m.	115		Znorow, Wessely, Moravia.
Found 1832.	116	1,891 258	WALKER COUNTY, Alabama, U. S. A.  Iron. Large etched slab. On under side and ends shows crust, and well-marked octahedral cleavage. The figures come between the Coahuila and the Butler (Bates Co.) irons. They most nearly resemble the Coahuila markings, but are coarser, and show more clearly the "Trias" of Tschermak. [Smith Collection.]  Exterior showing well-marked octa-
		150 5	hedral cleavage and what appear to be plates of Schreiberseit. One face polished and etched, looks very silvery, and shows well-defined markings on some portions of the surface. [Smith Collection.]
		159.5 84	* Like the previous specimen. [Smith Collection.]  * Thin, etched alab, showing no figures, but only a mottled surface. [Smith Collection. From C. U. Shepard.]
Fell 1833. Nov. 25, 6} p. m.	117		Blansko, Brünn, Moravia.
Found 1834.	118		LIME CREEK, CLAIBORNE (Monroe or Clarke Co.), Alabama, U. S. A.
Found 1884.	119	486	SCRIBA, OSWEGO Co., New York, U. S. A. Iron. Slab, showing on one side a curious fine-pitted surface. Etched face shows mottled surface in streaks, with two very thin Widmanstättian plates appearing in cross section at one place. Otherwise, no figures. [Smith Collection.]
Fell 1834. Jan. 8, 94 a. m.	120		OKNINY, VOLHYNIA, Russia.
Fell 1834. June 12, 8 a. m.	121	.5	CHARWALLAS, near Hissar, Delhi, India. Stone. Brown and white, with rusty iron grains. Polished face. [Smith Collection. From Professor Jameson of Edinburgh.  * Like previous specimen.
Found 1835.	122		BLACK MOUNTAIN, Buncombe Co., North Carolina, U. S. A.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1835. Jan. 81.	128		MASCOMBES, Corrèze, France.
Fell 1835. Aug. 1.	124	1,975 171 213.5	CHARLOTTE, DICKSON Co., Tennessee, U. S. A.  Iron. Large rounded mass, with smooth, unaltered exterior. Two polished faces. Shows beautiful Widmanstättian figures, fine, about like Obernkirchen. [Smith Collection.]  * Thin, polished slab, full section except for one end. [Smith Collection.]  * Block, consisting of three etched surfaces at right angles, and the rest crust. [Smith Collection.]
Fell 1835. Aug. 4, 44 p. m.	125	9	ALDSWORTH, CIRENCESTER, England. Stone. Polished rectangular slab, showing breccia-like structure of light-colored fragments in dark matrix, and occasionally large grains of iron. [Smith Collection.]
Fell 1835. Nov. 18, 9 p. m.	126		Belmont, Simonod, Ain, France. Probably not of meteoric origin.
Known 1886.	127	1,797	Wichita Co., Brazos River, Texas, U.S. A.  Iron. Full-sized slab, etched, showing most beautiful Widmanstattian figures and the three kinds of iron clearly defined, with the separate plates marked by fine Neumann lines. It also contains numerous large inclusions of troilite. [Purchased from Ward and Howell.]
Found 1836.	128		GREAT FISH RIVER, South Africa.
Fell 1836. Nov. 11, 5 a. m.	129	17.5	MACAO, Rio Grande do Norte, Brazil. Stone. Gray, with rusty iron grains, and dull black crust on one end. Polished surface shows a seam of silvery iron, with a most beautiful fine crystalline structure. [Smith Collection.]
Fell 1837. July 24, 111 A. M.	130		GROSS-DIVINA, Trentschin, Com. Hungary.
Fell 1837. August.	181		ESNANDES, Charente Inférieure, France.

Date of Fall or Find.	No.	Weight in Grams.	Description.
	132	317,500	BUTCHER IRONS, COAHUILA, Mexico. Complete individual, showing smooth crust, but in some places deeply pitted.
		158,800	[Smith Collection.]  * Like previous specimen. [Smith Collection.]
		249,500	* Like previous specimen. [Smith Collection.]
		23,000	Full-size slab, showing numerous inclusions of troilite. [Smith Collection.]
		22,310	* Complete individual, except for one polished face. [Smith Collection.]
		12,700	* Mass, with two faces cut at right angles. [Smith Collection.]
		21,886	Mass, with one polished face showing crack across the middle (600 cm. long) filled in with crust. [Smith Collection.]
		17,000 <b>4,</b> 536	* Slab. [Smith Collection.]  * Complete individual, except that
		3,640	one end has been cut off and polished.  [Purchased.]  * Three polished faces at right an-
			gles, the rest crust. [Purchased from Ward and Howell.]
		1,658	* Four cut faces at right angles, the rest crust. [Smith Collection.]  * Rounded mass, with two polished
			faces. [Smith Collection.]
		107.5 114.5 80.5 88	
		85.5 20	* Slabs showing Daubréelite. [Smith Collection.]
		16.5 14.5 14.5	
		119 102	* Shows crust. [Smith Collection.]
		86 75.5 72	
		66.5	* Slabs. Several of them etched, and
		65 65 63.5	some containing troilite. Also other small pieces. [Smith Collection.]
		63 66	
		40.5 38.5	

		W-1-1-4	
Date of Fall or Find.	No.	Weight in Grams.	Description.
		1,217	Etched slab. The Neumann lines appear at first sight like the markings on a chopping-block, without any definite direction, as shown in Fig. 3, which is printed directly from the specimen. A striking feature of the etched surface is the appearance at first of two sets of fine parallel lines, which become obliterated by the continued action of the acid. These lines can be made out near the lower right-hand corner of the figure. The more marked and coarser crystallization, appearing at the left, is unusual in the Coahuila specimens.
		1	A cleavage mass, broken out from a perfectly compact specimen of the above iron by quick blows of the hammer. This mass, shown of twice its natural size in Fig. 4, has the form of the cube twin described by Tschermak, as typical of the Hauptmannsdorf iron, with this difference, that the cube in this case is modified by the octahedron. On etching the faces, beautiful striations appeared, all parallel to edges either of the cube or octahedron. Most of these lines were so fine as to be microscopic, though a few were coarse enough to exhibit even under a pocket lens all the characters of Widmanstättian lines. On the octahedral face
		15	there were no regular striations.†  Another cleavage mass found in contact with the previous one, but having the form of an acute rhombic prism with an angle of about 120°. This prism, one etched face of which is shown of twice the natural size in Fig. 5, could only be separated by the hammer over the area abcd, and the rest of the face had to be continued by cutting through a very compact part of the specimen. ab, bc, and cd are the natural crystal edges. The upper figure was copied directly from the specimen, without any knowl-

<sup>†</sup> Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," Proceedings of the Am. Acad., Vol. XXI. p. 478. American Journal, 3d Series, Vol. XXXII. p. 284.

Date of Fall or Find.	No.	Weight in Grams.	Description.
			edge of the arrangement of the Neumann lines, but it was afterwards seen that they could all be referred to a cube with twin members on all the trigonal axes. The middle diagram shows such a cube face with the twinning lines, and the lower figure of the crystal was drawn from the diagram by means of a parallel ruler.†
Fell before 1888.	138		Simbirsk, Partsch, Russia.
Fell before 1838.	134		Slobodka, Partsch, Russia.
Fell 1838. Jan. 29.	135		KARE, Sandee District, Oude, India.
Fell 1888. April 18.	136	7	AKBURPUR, SAHARANPUR, India. Stone. Polished slab, showing breccia-like structure of light-colored fragments in black groundmass. Full of iron grains, and showing curious cellular black crust. [Smith Collection.]
Fell 1838. June 6, Noon.	187	15.5	CHANDAKAPUR, Beraar, India. Stone. Light gray, filled with rusty iron grains. Polished slab, with dull black crust on edges. [In exchange from S. C. H. Bailey.]
Fell 1838 July 22, Day.	138		MONTLIVAULT, Loire-et-Cher, France.
Fell 1838. Oct. 18, 9 a. m.	139	5.5 8 1.5 1	COLD BOKKEVELD, Cape of Good Hope, Africa. Stone. Dead black, with white specks but apparently no iron. Shows crust. [Smith Collection.]  * Like the previous specimen. [Smith Collection.]  * Also some fine powder.
Known 1839.	140		Baird's Farm, Asheville, North Carolina, U. S. A.

<sup>†</sup> Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

Found 1839.  141 2,112  PUTNAM COUNTY, Georgia, U. S. A.  Iron. Dropping to pieces from oxidation, but breaking up into perfectly regular octahedral fragments. [Smith Collection.]  * Mass showing crust, and perfect octahedral cleavage. [Smith Collection.]  A very perfect cleavage octahedron, one face of which is shown of double its natural size in Fig. 6. This octahedron was so loose in its structure that it was necessary to mount it in pitch before grinding the face, in order to prevent the plates from splitting off.  It will be noticed that at a, b, and c the spaces between the Widmanstättian plates are filled with a perfectly granular iron, and also that the entire mass is broken up, without reference to the crystalline plates, into irregular polygonal masses, suggesting its having been suddenly cooled from a condition of intense heat.†  * An acute rhombic prism with the faces etched, showing beautiful Widmanstättian plates arranged parallel to the regular octahedron.  * Octahedral fragments.  Fell 1839.  Fell 1839.  Fell 1839.  Fell 1839.  Indicate the face of which is shown of the surface show regular and considerable iron.  [Smith Collection.]  Cosby's Creek, Cocke Co., Tennessee, U. S. A.  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abundable in the collection of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abundable in the property of the surface show regular and considerable iron in the collection of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appe	Date of Fall or Find.	No.	Weight in Grams.	Description.
* Mass showing crust, and perfect octahedral cleavage. [Smith Collection.]  A very perfect cleavage octahedron, one face of which is shown of double its natural size in Fig. 6. This octahedron was so loose in its structure that it was necessary to mount it in pitch before grinding the face, in order to prevent the plates from splitting off.  It will be noticed that at a, b, and c the spaces between the Widmanstättian plates are filled with a perfectly granular iron, and also that the entire mass is broken up, without reference to the crystalline plates, into irregular polygonal masses, suggesting its having been suddenly cooled from a condition of intense heat.†  * An acute rhombic prism with the faces etched, showing beautiful Widmanstättian plates arranged parallel to the regular octahedron.  * Octahedral fragments.  PINE BLUFF, LITTLE PINEY, Missouri, U. S. A.  Stone. Thin slab, light gray with darker grains and considerable iron. [Smith Collection.]  COSBY'S CREEK, COCKE Co., Tennessee, U. S. A.  12,750  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abun-	Found 1889.	141	2,112	Iron. Dropping to pieces from oxidation, but breaking up into perfectly regular octahedral fragments. [Smith
A very perfect cleavage octahedron, one face of which is shown of double its natural size in Fig. 6. This octahedron was so loose in its structure that it was necessary to mount it in pitch before grinding the face, in order to prevent the plates from splitting off.  It will be noticed that at a, b, and c the spaces between the Widmanstättian plates are filled with a perfectly granular iron, and also that the entire mass is broken up, without reference to the crystalline plates, into irregular polygonal masses, suggesting its having been suddenly cooled from a condition of intense heat.†  * An acute rhombic prism with the faces etched, showing beautiful Widmanstättian plates arranged parallel to the regular octahedron.  * Octahedral fragments.  * PINE BLUFF, LITTLE PINEY, Missouri, U. S. A.  Stone. Thin slab, light gray with darker grains and considerable iron.  [Smith Collection.]  * COSEY'S CREEK, COCKE Co., Tennessee, U. S. A.  12,750  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abun-			178	* Mass showing crust, and perfect
been suddenly cooled from a condition of intense heat.†  * An acute rhombic prism with the faces etched, showing beautiful Widmanstättian plates arranged parallel to the regular octahedron.  * Octahedral fragments.  PINE BLUFF, LITTLE PINEY, Missouri, U. S. A.  Stone. Thin slab, light gray with darker grains and considerable iron.  [Smith Collection.]  COSET'S CREEK, COCKE Co., Tennessee, U. S. A.  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abun-			8	A very perfect cleavage octahedron, one face of which is shown of double its natural size in Fig. 6. This octahedron was so loose in its structure that it was necessary to mount it in pitch before grinding the face, in order to prevent the plates from splitting off.  It will be noticed that at a, b, and c the spaces between the Widmanstattian plates are filled with a perfectly granular iron, and also that the entire mass is broken up, without reference to the crystalline plates, into irregular poly-
U. S. A. Stone. Thin slab, light gray with darker grains and considerable iron. [Smith Collection.]  Cosby's Creek, Cocke Co., Tennessee, U. S. A.  12,750  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstattian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abun-				of intense heat.†  * An acute rhombic prism with the faces etched, showing beautiful Widmanstättian plates arranged parallel to the regular octahedron.
U. S. A.  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstattian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abun-		142	8	U. S. A. Stone. Thin slab, light gray with darker grains and considerable iron.
tions of the surface are entirely free	Described 1840.	143	12,750	U. S. A.  Mass with one polished face, showing great variation in structure. Portions of the surface show regular and well-marked Widmanstättian figures, while other parts show only irregular polygonal masses with no appearance of crystalline structure. Moreover, bright nickeliferous iron appears abundantly in some places, while other por-

<sup>†</sup> Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

Date of Fall or Find,	No.	Weight in Grams.	Description.
		451	from it. The exterior shows a very striking octahedral structure, and the plates are separated by a thick foil of Schreiberseit, which can be easily detached from the iron. [Smith Collection.]  One polished face, showing characteristic Widmanstättian figures, with sections of bright nickel iron. The exterior shows very striking octahedral structure, and several of the octahedral faces have been polished and etched, showing no figures. Contains a very large nodule of troilite. [Smith Collection.]
	140	7,710	SEVIER COUNTY, found in 1845, but evidently identical with Cocke County.  Mass with two cut faces, one face containing a large nodule of graphite.  The exterior shows beautiful octahe-
		70	dral structure. [Smith Collection.] Nodule of graphite, formerly weighed 80 grams, but has been cut. Also nu-
		711	merous other nodules of graphite, and troilite. [Smith Collection.]  Complete individual, containing a large nodule of graphite, and showing all the characteristic structure of the Cocke County iron. This specimen was presented to the Cabinet by Prof. N. S. Shaler, and is reported to have come from Lebanon Co., Tennessee, but is evidently the same as the Sevier and Cocke County irons.
Found 1840.	144	9,980	CONEY FORK, CARTHAGE, SMITH Co., Tennessee, U. S. A.  Iron. Large mass of cleavage octa- hedrons, with sharply defined faces and edges, packed together like an aggre- gate of large crystals of alum. [Smith
		932	Collection.]  This specimen shows six faces of a rough octahedron, one of the faces having an area of seven square inches. One half of this octahedron has been partially torn apart into numerous smaller crystals, some of them an inch or more in diameter; but though the crevasses between the individuals are in some places nearly a quarter of an

Date of Fall or Find.	No.	Weight in Grams.	Description.
		5,705	inch in breadth, yet they are bound firmly together by a network of plates, which in some parts raggedly jut out from the octahedral faces. The general appearance of the exterior of the specimen reminds one somewhat of a rough mass of galena crystals, only of octahedral form. The rough crystal is evidently the result of fracture, probably caused during the passage of the mass through the air, and the octahedral faces are cleavage planes, if the term cleavage may be applied to such fractures, which cannot be reproduced by splitting in the ordinary way on account of the malleability of the mass. The specimen further exhibits a fused crust over the octahedral faces, which must have formed after the partial breaking up of the large mass, giving a rounded appearance to the edges. On a polished surface, cut nearly parallel to the largest octahedral face, the figures produced by etching appear very strikingly. They are perfectly distinct and regular, being typical Widmanstättian figures; but when they come to the cracked portion of the iron, they appear as separate plates, some having been broken by the rupture, others separated, while the greater number appear bent and strained, but still coherent and binding the mass firmly together. The whole appearance on the etched surface gives at once the idea of a forcible explosion, and yet all the cracks, even the most ragged, follow directions parallel to the octahedral faces.† [Smith Collection.]  Specimen with three faces at right angles to each other polished and etched. The exterior is ragged, with octahedral plates jutting out. [Smith Collection.]
		186.5	This specimen consists of a mass of octahedral plates loosely packed together so as to form hopper crystals. In

† Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

Date of Fall or Find.	No.	Weight in Grams.	Description,
Found 18 <b>4</b> 0.	145	159 118 86 62 50 48.5 9.5	the Smith Collection it bears the label "Smithland, Lincoln Co., Tenn.," but appears identical with the Coney Fork specimens.  * Polished slab, containing a large nodule of troilite. Crust on edges.  [Smith Collection.]  * Slab, with both sides highly polished. [Smith Collection.]  * Polished slab. [Smith Collection.]  * Etched slab. Crust on edge.  [Smith Collection.]  * Polished slab. [Smith Collection.]  * Very thin slab. [Smith Collection.]  Piece consisting of a single set of parallel plates.  Petropavlovsk, Mrass, Tomsk, Siberia.
Found 1840.	146	2,287 782 281.5	CAREYFORT, DE KALB Co., Tennessee, U. S. A.  Iron. Two surfaces, cut at right angles and etched, show typical Widmanstättian figures. One face contains a large nodule of troilite, the rest crust. [Smith Collection.]  This specimen shows hollow octahedral faces, two inches in diameter, like hopper crystals, consisting of skeletons built up of a series of plates about half an inch wide and one sixteenth of an inch thick. These plates, when cut transversely, constitute the Widmanstättian figures. When the section is cut at random, the figures may differ somewhat in character, and the plates appear to make various angles with each other; but when the etched surface is parallel to an octahedral face, the Widmanstättian figures all make equilateral triangles, their sides being parallel to the octahedral edges. Fig. 7 shows of original size an etched surface of this specimen cut parallel to an octahedral face. [Smith Collection.]  Shows crust and three etched faces. [Smith Collection.]  *Shows crust and two cut faces. [Smith Collection.]

	T		
Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1840.	147	208	MAGURA, SZLANICZA, ARVA, Hungary. Iron. One polished face. Rest of surface covered with crust. [Smith Col-
·		185	lection.]  Three faces at right angles to each other, etched, showing that the character of the Widmanstattian figures varies greatly with the direction in which the face is cut. In some cases the figures are very regular, and are largely made up of a bright nickeliferous iron, though in some cases the bright iron is wholly absent and the figures are replaced by irregular cracks. [Smith
		185	Collection.] Three etched faces. Elsewhere surface covered with crust. [Smith Collection]
		141	lection.]  * Slab, with both faces etched, showing most perfect figures. Crust on
		93.5	edge. [Smith Collection.]  * One etched face. Rest of surface covered with crust. [Smith Collection.]
		38 64	Thin slab, with crust on edge. Shows no well-defined figures. [Purchased from Ward and Howell.]  Appears to be a lump of altered crust. [Smith Collection.];
Found 1840.	148	1,828	SMITHLAND, LIVINGSTON Co., Kentucky, U. S. A. Iron. One etched face. No figures. The other portions of the specimen are covered with a very deeply pitted crust.
		456 93	[Smith Collection.] Three polished faces at right angles to each other, and the rest showing crust, deeply pitted. [Smith Collection.] Has been forged. [Smith Collection.]
Found 1840.	149	137 } 52 }	TARAPACA, HEMALGA, Chili. Evidently cast-iron. [Smith Collection. From C. U. Shepard.]
Fell 1840. May 9, Noon.	150		KARAKOL, Ajagus, Russia.
Fell 1840. June 12, 104 A. E.	151		STAARTJE, UDEN, Holland.
Fell 1840. July 17, 71 a. m.	152		CERESETO, CASALE, Monferrate, Piedmont.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1841. March 22, 81 r. m.	158		Gröneberg, Heinrichsau, Prussian Silesia.
Fell 1841. June 12, 1½ r. m.	154	50.5 27 .5 } }	CHÂTRAU-RENARD, Loiret, France. Stone. Irregular fragment of dark gray stone, sprinkled through with specks of iron, and intersected by numerous cracks filled with fused crust.  [Purchased from Ward and Howell.]  Fragment showing dull black crust.  [Smith Collection.]  * Fragments. [Purchased from the Liebener Collection.]  * Minute fragments. [Smith Collection.]
Fell 1842. April 26, 8 p. m.	1 <b>5</b> 5	77.5 6	tion.]  Pusinsko Selo, Milena, Croatia.  Stone. Light gray, with dull black crust. Polished face shows large grains of iron. [Smith Collection.]  *Fragment with one cut face. [Smith Collection.]
Fell 1842. June 4.	156	2	AUMIÈRES, Lozère, France.  * Stone. Very light gray with silvery specks of iron, and intersected by a dark vein. [Smith Collection.]  Same, but showing a thin round plate of iron 6 mm. in diameter. [Smith Collection.]  * Several smaller fragments, and some sand. [Smith Collection.]
Fell 1842. July 4.	157		Barea, Logroño, Spain.
Known 1843.	158		St. Augustine's Bay, Madagascar.
Fell 1848. March 25.	159	48 4.5 }	BISHOPVILLE, South Carolina, U. S. A. Stone. White and gray, with smooth, vitreous gray and white crust. Looks like a partially decomposed silicate. [Smith Collection.] * Fragments. [In exchange from C. U. Shepard.]
Fell 1848. June 2, 8 p. m.	160	9	UTRECHT, Holland. Stone. Light gray with darker grains, and dull black crust. Polished face, showing iron grains. [Smith Collection.]
Fell 1843. June 29, 81 P. M.	161		Manegaum, near Eidulabad, India.

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Date of Fall or Find.	No.	Weight in Grams,	Description.
Fell 1848. Sept. 16, 47 p. m.	162		KLEIN WENDEN, Erfurt, Prussia.
Fell 1843. Nov. 12.	168		VEREHNE TSCHIRSEAJA, Don, Russia.
Fell 1844. Jan., 11 a. m.	164		CERRO COSIMA, Dolores Hidalgo, Mexico.
Fell 1844. April 29, 8} r. m.	165		KILLETER, County Tyrone, Ireland.
Fell 1844. Oct. 21, 62 a. m.	166		FAVARS, Aveyron, France.
Fell 1845. Jan. 25, 8 p. m.	167	8.5	LE PRESSOIR, LOUANS, Indre-et-Loire, France. Stone. Light gray, with iron grains.
Fell 1845 ?	168		BARATTA, Deniliquin, New South Wales.
Fell 1845. July 14, 8 p. m.	169		LA VIVIONNÈRE, LE TEILLEUL, Manche, France.
Fell 1846. August 14, 8 p. m.	170	·	CAPE GIRARDEAU, Missouri, U. S. A.
Described 1846.	171		Jackson Co., Tennessee, U. S. A.
Found 1846.	172		Netschaëvo, Tula, Russia.
Found 1846.	178		Assam, India.
Fell 1846. May 8, 9} a. m.	174		Monte Milone, Macerata, Italy.
Fell 1846. Dec. 25, 24 p. m.	175		Schönenberg, Swabia, Bavaria.
Found 1847.	176	1,476 580 115.5 79 78)	MURFREESBORO, RUTHERFORD Co., Tennessee, U. S. A. Iron. Rectangular block, with crust on the ends. Shows very marked, typical Widmanstättian figures. [Smith Collection.]  Mass, formed by five natural octahe- dral faces and two cut surfaces. [Smith Collection.]  * Three polished faces, at right an- gles, the rest crust. [Smith Collection.]  * Etched slab, with crust on one end. Shows beautiful Widmanstättian fig- ures. [Smith Collection.]  * Etched slabs similar to the previous specimen. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1847.	177		CHESTERVILLE, Chester Co., South Carolina, U. S. A.
Found 1847.	178	706	SEELÄSGEN, Brandenburg, Prussia.  Iron. Shows curious irregular granular structure on natural fracture. A face polished and etched shows the same granular structure, only with here and there a Widmanstättian plate.
•		248	[Smith Collection. From C. U. Shepard.]  * Etched slab. Crust on ends. [Smith Collection. From C. U. Shepard.]
Fell 1847. Feb. 25, 24 a. m.	179	203.5	HARTFORD, LINN Co., Iowa, U. S. A. Stone. Light gray, full of iron grains, and intersected with cracks filled with crust. Dull black finely pitted crust on three sides, all in differ- ent degrees of fusion. One polished face. [Smith Collection.]
		167.5	* Irregular fragment, showing crust.
		8.5	[In exchange from C. U. Shepard.]  * And other small fragments.
Fell 1847. July 14, 8} A. M.	180	80	Braunau, Hauptmannsdorf, Bohemia.  Iron. Beautiful etched slab, showing Neumann lines, some of which are sufficiently coarse to show under a lens all the features of Widmanstättian figures. Shows crust, and also cubic cleavage. [Smith Collection. From Wöhler.]
		82	Block showing cleavage. [Smith Collection.]
		80	Block showing cleavage and crust. An etched face of one of the cleavage crystals is shown enlarged in Fig. 8. At a appears the face of a twin cube and the diagonals parallel to the intersection edge followed the same twin on an adjacent face, showing that they were twinning lines, and not lines of octahedral or dodecahedral faces. The lines appearing parallel to the cube edges proved to belong to the simple cube.†  [Smith Collection.]
		18.5	Shows cleavage and crust. [Smith Collection.]

† Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1848. May 20, 41 a. m.	181	.5	CASTINE, Hancock Co., Maine, U. S. A. Stone. Light gray, with iron grains. [Smith Collection.]
Fell 1848. July 4.	182		MARMANDE, Aveyron, France.
Fell 1848. Dec. 27, Evening.	183		SKI, AKERSHUUS, Norway.
Found 1849.	184		Morgan Co., Alabama, U. S. A.
Fell 1849. Oct. 31, 8 r. m.	185	168	Monroe, Cabarras Co., North Carolina, U.S. A. Stone. Dark gray with light grains, and thickly sprinkled with iron. Fragment, showing dull black crust. [Smith Collection.]
•		8.5	* Highly polished slab. [In exchange from C. U. Shepard.]
Described 1850.	186	448	RUFF'S MOUNTAIN, LEXINGTON Co., South Carolina, U. S. A.  Iron. Slab, etched, showing well-marked Widmanstättian figures, only there is a curious indefiniteness about them, which is very characteristic. Shows crust. [Smith Collection. From
		127.5	C. U. Shepard.]  Similar to previous specimen. [In exchange from C. U. Shepard.]
Described 1850.	187	84	PITTSBURG, Alleghany Co., Pennsylvania, U. S. A. Iron. A ragged end, showing on the exterior a well-marked octahedral structure, but on an etched surface there is only a mottled appearance, except in one corner, where broad, typical, Widmanstättian figures appear. [Smith Collection.]
Described 1850.	188	804	SALT RIVER, Kentucky, U. S. A. Iron. Crust, and three etched surfaces, which in some places only present a mottled appearance, while in other parts there are very fine, and somewhat indistinct, Widmanstattian figures. [Smith Collection.]
Found 1850.	189	81.5	SCHWETZ, Prussia. Iron. Thin slab with crust on edges. One face etched, showing well-marked

Date of Fall or Find.	No.	Weight in Grams,	Description.
			Widmanstättian figures. [Smith Collection. From C. U. Shepard.]
Found 1850.	190	10	SENECA FALLS, Seneca River, New York, U. S. A. Iron. Etched slab, showing very well marked Widmanstattian figures, also octahedral cleavage. Crust on edge of slab. [Smith Collection.]
Found 1850.	191	10	MAINZ, Hesse, Germany. Stone. Irregular brown fragment, apparently a piece of the crust. [Smith Collection.]
Fell 1850. Nov. 30, 44 p. m.	192	8	SHALKA, BANCOORAH, Bengal, India. Stone. Light gray and black fragment with iron grains, and veins filled with black crust. [Smith Collection.]
Recognized 1851.	198	211.5	AINSA (The SIGNET-IRON), SONORA, Tucson, Arizona, U.S.A. Iron. Slab, with crust on edges. [In exchange from U.S. National Museum.]
		25	<ul> <li>Thin, etched slab, showing no figures but a granular arrangement brought out by the acid. [Smith Col-</li> </ul>
		17	lection.]  * Irregular piece, showing crust.  [Smith Collection.]  * Also a quantity of turnings. [Presented by Prof. B. Silliman.]
Fell 1851. April 17, 8 p. m.	194		Götterslon, Minden, Westphalia, Prussia.
Fell 1851. Summer.	195		Quinçay, Vienne, France.
Fell 1851. Nov. 5, 5‡ P. M.	196		Nulles, Catalonia, Spain.
Found 1852.	197	16	CRANBERRY PLAINS, POPLAR HILL, Virginia, U. S. A.  Iron. A very perfect octahedron, two etched faces of which are shown in Fig. 9 of original size. It will be seen by this sketch that the octahedral outline has been sharply formed; but while many of the Widmanstättian plates are parallel to this outline, there

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Date of Fall or Find.	No.	Weight in Grams.	Description.
		7.5 7 5.5	are others which are markedly curved. These curved plates must have originally formed through the liquid mass as true planes, like their neighbors, and have been bent in the subsequent solidifying of the remaining material. For, if they had been distorted by an exterior force, the regularity of the octahedron would have been at the same time destroyed.†  * Thin slab, with crust on edges. [Smith Collection.]  * Same as the previous specimen. [Smith Collection.]
Fell 1852. Jan. 23, 43 p. m.	198	64 85.5	YATOOR, NELLORE, Madras, India.  Stone. Gray, with three polished faces showing considerable iron. Dull, black crust, and also crust partially formed. [Smith Collection.]  *Four polished faces and crust.
		60.5	[Smith Collection.]  * Two small fragments, weighing half a gram each. [Smith Collection.]
Fell 1852. Sept. 4, 44 p. m.	199	51	FERETE, MEZŐ-MADARÁS, Transylvania. Stone. Dark rock, with light-colored grains surrounded by iron. One face polished. Dull, black crust on two sides. [Smith Collection. From C. U. Shepard.]
		22.5	Polished slab. [By exchange with ] C. U. Shepard.]
Fell 1852. Oct. 18, 8 p. m.	200		BORKUT, MARMAROS, Hungary.
Fell 1852. Dec. 2.	201	12	Buster, near Goruckpur, India. Stone. White, with black and white crust. Perfect cleavage with pearly lustre, looking like partially decom-
		8.5	posed felspar. [Smith Collection.] Polished block, showing round, pink grains. [Smith Collection.]
		2	* Like previous specimen.

<sup>†</sup> Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

Date of Fall or Find.	No.	Weight in Grams,	Description.
			* Also two small fragments showing the pink grains. [Smith Collection.]
Known 1853.	202		Lion River, Great Namaqualand, South Africa.
Found 1853.	208	381.5 105.5 47 81 5 2.5 4 2.5 2.5 1.5	KNOXVILLE, TAZEWELL Co., Tennessee, U. S. A.  Iron. Showing most beautiful and very minute octahedral structure. Fig. 10 shows very roughly an exact sketch, the original size, of an etched face of this specimen. There is almost no limit to the fineness of some of the Widmanstättian figures.† [Smith Collection.]  * One cut face. Rest of surface covered with crust. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]  * Etched face, crust, and fresh fracture, showing beautiful octahedral cleavage. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]  * Etched slabs. [Smith Collection.]  Fragment, in layers of plates. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]  * And other small fragments.
Found 1858.	204	24 4 7	UNION COUNTY, Georgia, U. S. A.  Iron. Appears to be mostly crust. Shows octahedral cleavage. [Smith Collection.]  Small plate. [Smith Collection.]  In small fragments. [Smith Collection.]

<sup>†</sup> Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

f	7		<del>                                     </del>
Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1853.	205	27.5	STINKING CREEK, CAMPBELL Co., Tennessee, U. S. A.  Iron. Appears to be a complete individual except where a corner has been broken off, showing an irregular fracture. Has holes running through the mass. An etched surface shows a network of fine, irregular, silvery lines, but no figures. [Smith Collection.]
Fell 1853. Feb. 10, 1 p. m.	206	20.5	GIRGENTI, Sicily. Stone. Gray, fine-grained with iron specks. Dull black crust, and intersected by heavy veins filled with fused crust. [Smith Collection.]
Fell 1853. March 6.	207	118.5	SRGOWLEE, Bengal, India. Stone. Brown and rusty looking, with smooth brown crust. One large polished face shows considerable iron,
		6.5	and also troilite. [Smith Collection.]  • Irregular fragment, showing crust. [Smith Collection.]
Fell 1853. March 6.	208	.5 .5	DURUMA, Wanikaland, East Africa. Stone. Gray, rusty-looking fragment, with smooth dark brown crust.  * Same, but without crust.
Known 1854.	209	106	Jewell Hill, Madison Co., North Carolina, U. S. A.  Iron. Etched face, showing most beautiful, fine Widmanstättian figures,
[		15.5	also crust. [Smith Collection.]  * Slab, with crust on edge. [Smith
1		19	Collection.] Mass showing octahedral fracture.
		11.5	[Smith Collection.]  * Slab, with crust on edge. [Smith Collection.]
Known 1854.	210	1.5	OCRTIBBEHA COUNTY, Mississippi, U.S. A. Iron. Square block, etched but showing no figures. [Smith Collection.]
		8	Irregular fragment. [Smith Collection.]
Found 1854.	211	10	EMMETSBURG, Maryland, U.S. A. Iron. Thin slab, etched, showing well-marked Widmanstättian figures. [In exchange from S. C. H. Bailey.]

Date of Fall or Find.	No.	Weight in Grams,	Description,
Found 1854.	212	66	Madoc, Upper Canada.  Iron. Thin slab, etched, showing well-marked Widmanstattian figures with many of the plates bent. Crust on edges. [Smith Collection.]
		20	• Similar to previous specimen.  [Purchased from the Liebener Collection.] • Also a few turnings.
Found 1854.	213		VERKHNE-UDINSK (Niro River), Vitim, Siberia.
Found 1854.	214	283 186 34.5 27.5	CRANBOURNE, MELBOURNE, Victoria, Australia.  Iron. Apparently crust, looking like hematite, with chloride of iron exclusions. [Smith Collection.]  Like previous specimen. [Smith Collection.]  Crust, but with plates of Schreiberseit. [Smith Collection.]  Mass of iron with ragged exterior and one polished face, showing very broad perfect Widmanstattian figures. [Smith Collection.]
Found 1854.	215		TABARZ, near Gotha, Saxony.
Found 1854.	216	448.5	SAREPTA, Saratov, Russia.  Iron. One face polished and etched, the rest of the surface showing a deeply pitted crust. The Widmanstattian figures are very striking, exhibiting very broad plates, most beautifully marked with Neumann lines, and interspersed with plates of brilliant nickeliferous iron, unequally distributed over the surface. Something like the Wichita iron. [Smith Collection.]
Described in 1854.	217		HAYWOOD COUNTY, North Carolina, U. S. A.
Fell 1854. Sept. 5.	218		LINUM, Ferbellin, Prussia.
Fell 1855. May 11, 34 r. m.	219		OESEL, KAANDE, Livland, Baltic Sea.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1855. May 18, 5 p. m.	220	1 1 .5 .5	GNARRENBURG, BREMERVÖRDE, Hanover. Stone. Dark gray, with white grains and dull black crust. Little iron. [Smith Collection.] Fragment, without crust. [Smith Collection.] Fragment, with crust. [Smith Collection.] Same, without crust. [Smith Collection.] Other small bits.
Fell 1855. June 7, 73 P. M.	221		SAINT DENIS-WESTREM, near Ghent, Belgium.
Fell 1855. Ang. 5, 8½ P. M.	222	11 8	Petersburg, Lincoln Co., Tennessee, U. S. A. Stone. Gray, with dark gray, white, and light green grains. Very little iron. Shows shiny black crust, with raised veins, like the markings left on an oily surface by the palm of the hand. [Smith Collection.]  Small fragments, many of them showing crust. [Exchanged with C. U. Shepard.]
Known 1856.	228	50 8	DENTON COUNTY, Texas, U. S. A.  Iron. Rough exterior showing octa- hedral cleavage. Three polished faces, one of them etched, showing good Wid- manstättian figures. [Smith Collection.]  * Irregular fragment. [Smith Collec- tion.]
Known 1856.	224	32	ORANGE RIVER, Garib, South Africa.  Iron. One etched face, showing typical Widmanstättian figures. The rest of surface covered with crust. Octahedral cleavage. [Smith Collection.]
Found 1856.	225	85.5 28	FORT ST. PIERRE, NEBRASKA, U. S. A. Iron. Etched slab, showing good' Widmanstattian figures. Also crust. [Smith Collection.] One polished face. The rest of surface covered with crust. [Smith Collection.]
Found 1856.	226	2,800	NELSON COUNTY, Kentucky, U. S. A. Iron. Very thick slab, full section, with two polished faces. Etched. The

Date of Fall or Find.	No.	Weight in Grams.	Description.
			exterior appears very smooth except at one end, where it is very ragged, as if torn apart by an explosion when in a slightly plastic condition. On the etched face Widmanstättian figures appear in unusually broad plates and perfectly distinct, but they entirely fade out towards the edges, and wholly disappear near the ragged end of the specimen. [Smith Collection.]
Found 1856.	227	95.5 30 15.5	HAINHOLZ, MINDEN, Westphalia.  Stone. Dark brown. Polished face shows iron and olivine about equally distributed. Drops of chloride of iron on exterior. [Smith Collection.]  Same as previous specimen. [Smith Collection.]  Same as previous specimen. [Smith Collection.]  Two polished faces showing larger nodules of olivine than previous specimens. [In exchange from C. U. Shepard.]
Found 1856.	228		Forsyth, Taney Co., Missouri, U.S. A.
Fell 1856.	229		Avilez, Durango, Mexico.
Fell 1856. August 5.	230		Ovirdo, Asturia, Spain.
Fell 1856. Nov. 12, 4 p. m.	281		Trenzano, Brescia, Italy.
Found 1857.	232		LAURENS COUNTY, South Carolina, U. S. A.
Fell 1857. Feb. 28, Noon.	288	90 44 7 1	PARNALLEE, MADRAS, India.  Stone. Dark gray, with large white, dark gray, and brown grains. Dull black crust, and polished face, showing specks of iron distributed through the mass. [Smith Collection.]  * Irregular fragment. [Smith Collection.]  * Fragment, with crust. [Gift of B. Silliman, Jr.]  * Fragment, with crust. [Smith Collection.]  * And other small fragments showing crust. [Smith Collection.]

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1857. Mar. 24, 5 p. m.	234		STAVROPOL, Caucasus, Russia.
Fell 1857. April 1, Night.	285		HEREDIA, SAN JOSÉ, COSTA RICA, Central America.
Fell 1857. April 15, 10} p. m.	236	1	KABA, DEBRECZIN, Hungary. Stone. No iron. Black, with white specks. [Smith Collection.]
Fell 1857. Oct. 1.	237		LES ORMES, Yonne, France.
Fell 1857. Oct. 10, 12 p. m.	238	80.5	VERESEGYHÁZA, OHABA, Blasendorfer, Hungary. Stone. Polished slab. Dark gray, with large amount of iron, and dull black crust on edges. [Smith Collec- tion.]
Fell 1857. Dec. 27, 21 A. M.	239	1	Prou (Quenggouk), British Burmah. Stone. Very light gray fragment, with specks of iron. [Smith Collection.]  Also some small bits in a bottle. [Purchased from Liebener Collection.]
Known 1858.	240	<b>3</b> <b>3</b> .5	WAYNE COUNTY, near WOOSTER, Ohio, U.S. A. Iron. Thin slab, etched, showing typical Widmanstättian figures. [Smith Collection.]  * Irregular fragment. [Smith Collection.]
Found 1858.	241	8	ATACAMA, BOLIVIA, South America. Iron. Fragment with crust. One cut face, etched, showing well-marked Widmanstättian figures. [Smith Collection.]
Found 1858.	2 <del>1</del> 2	1,627 2,743 225	STAUNTON, AUGUSTA Co., Virginia, U. S. A. Iron. Full section slab, beautifully polished. [Purchased of Ward and Howell.] Found in 1870. Full section slab, polished, and containing a nodule of troilite 5 cm. in its longest dimension. [Smith Collection.] Found in 1870. Etched slab, showing well-marked Widmanstattian fig-
			ures. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1858.	243	3,634	TRENTON, WASHINGTON Co., Wisconsin, U. S. A.  Iron. One cut face, the rest crust deeply pitted. Shows good octahedral cleavage, the plates being separated by a thin foil of Schreiberseit, which is
		1,045	readily detached from the iron. [Smith Collection.]  Block, polished on four sides, the rest crust. Contains a large nodule of troilite. [Smith Collection.]
		863.5	<ul> <li>Block, with four polished faces, and the rest crust. Contains a large</li> </ul>
		363.5	nodule of troilite having a breccia-like structure. [Smith Collection.]  * Block, with four cut faces and the rest crust. [Smith Collection.]
		105.5	• Polished slab with crust on edges. Shows Widmanstättian figures even
		91	before etching. [Smith Collection.]  • Highly polished slab, with crust. [Smith Collection.]
		72.5	* Similar slab, with a large nodule of troilite. [Smith Collection.]
		60 } 14.5 }	* Similar slabs. [Smith Collection.]
Fell 1858. May 19, 8 a. m.	244	1	KAKOWA, Temeser Banat, Hungary. Stone. Gray, with darker grains, and dull black crust. [Smith Collection.]
Fell 1858. Dec. 9, 7} a. m.	245	210	Ausson, Montrejeau, Haute-Garonne, France. Stone. Gray, with darker grains
		-10	and rusty iron particles. [Purchased of Louis Saemann.]
		60	* Irregular fragment. [Smith Collection.]
1		43	• Irregular fragment. [Smith Collection.]
		1	• Irregular fragment. [Smith Collection.]
Fell 1858.	246		Molina, Murcia, Spain.
Described 1859.	247		CZARTORYA, ZABORZIKA, Volhynia, Russia.
Found 1859.	248		PORT ORFORD, Rogue River Mts., Oregon, U. S. A.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1859. Mar. 28, 4 P. M.	249	85	HARRISON COUNTY, Indiana, U. S. A. Stone. Nearly a complete individual, with dull brown, finely pitted crust. Fracture appears light gray, set through with coarse dark gray fragments, and specks of iron. [Smith Collection.]
Fell 1859. April 4.	250		MEXICO, District of PAMPANGA, Luzon, Philippine Islands.
Fell 1859. May 1, 8 p. m.	251		BUESTE, near Pau, Basses-Pyrénées, France.
Fell 1859. Aug. 11.	252		BETHLEHEM, near Albany, New York, U. S. A.
Described 1860.	258	60.5 57.5	MARSHALL COUNTY, Kentucky, U. S. A.  Iron. Thin slab, with crust on edges, showing good octahedral cleavage. Well-marked Widmanstättian figures are brought out with some difficulty on the etched surface. [Smith Collection.]  One etched face. The rest crust. [Smith Collection.]  Polished slab. Crust on edges. [Smith Collection.]
Known 1860.	254	1,300	Coopertown, Robertson Co., Tennessee, U. S. A.  Iron. Two faces at right angles, etched, showing beautiful Widmanstättian figures. The rest covered with crust, a natural octahedral cleavage appearing in one place.  Fig. 11 shows of original size the two etched faces, the larger one being parallel to an octahedral face determined by cleavage, and the other being at right angles. Most of the plates, forming in section equilateral triangles, are parallel to octahedral faces; but the plates marked b, and those parallel to them, bisect the octahedral angles and must be parallel to a dodecahedron. Moreover, the plates marked a, which are parallel to a lateral edge of the octahedron, when followed on to the face at right angles to the first continue to be parallel to the lateral edge, and therefore cannot be octahedral plates, and since they are parallel to a principal section of the octahedron they must be

No.	Weight in Grams,	Description.
	333.5 ) 145 ) 126.5 ) 85 49.5 25.5	cubic. Hence this specimen exhibits distinctly octahedral, dodecahedral, and cubic plates.† [Smith Collection.]  * Sawed slabs, with crust. [Smith Collection.]  * Etched slab. [Smith Collection.]  * Etched slab. [In exchange from C. U. Shepard.]  * Looks as if it had been through a forge. [Purchased from Liebener Collection.]
255	196.5	LAGRANGE, OLDHAM Co., Kentucky, U.S.A. Iron. Block with three cut faces, one of them etched, the rest crust. Shows very narrow and somewhat indistinct Widmanstättian plates. [Smith Collection.]
256	104	NEWTON COUNTY, Arkansas, U. S. A. Stone. Mostly olivine, with large grains of iron. One polished face. Rest of surface crust. Similar to Hainholz. [Smith Collection.] Polished slabs. [Smith Collection.]
257		DESERT OF ATACAMA, South America.
258	9	ALESSANDRIA (San Giuliano Vecchio), Piedmont, Italy. Stone. Gray, with dull black crust, and cracks filled with iron. [Purchased from Liebener Collection.]
259		KHIRAGURH, S. E. of Bhurtpur, India.
260	23,030 5,895	New Concord, Muskingum County, Ohio, U. S. A. Stone. A complete individual, somewhat angular, but covered with a dull black crust, and deeply pitted. [Smith Collection.]  * One polished face, showing considerable iron, and gray color, the rest of surface nearly completely covered with crust. [Smith Collection.]
	255 256 257 258	No. in Grams.  333.5   145   126.5   85   49.5   25.5    255   196.5    256   104   8   6   8    257   258   9    259   260   23,030

<sup>†</sup> Oliver W. Huntington "On the Crystalline Structure of Iron Meteorites," loc. cit.

Date of Fall or Find.	No.	Weight in Grams.	Description.
		800	One polished face and crust. [Smith
		136.5	Collection.]  Nearly covered with crust. [Smith Collection.]
			* Also numerous small fragments.  [Purchased from Liebener Collection.]  Also part of railroad sleeper fractured by the fall of the meteorite.
Fell 1860. June 16, 5 a. m.	261		Kusiali, Kumaon, India.
Fell 1860. July 14, 24 P. M.	262	542	DHURMSALA, Kangra, Punjaub, India. Stone. Gray, with rusty iron grains and dull black crust, deeply pitted.
		4	[Smith Collection.]  * Fragment showing crust, and with one polished face. [Smith Collection.]
Found 1861.	263		Heidrlberg, Baden, Germany.
Fell 1861. May 12.	264		Butsura, Goruckpur, India.
Fell 1861. May 14, 1 p. m.	265		CANELLAS, Villanova de Sitjes, near Barcelona, Spain.
Fell 1861. June 28, 7 p. m.	266		Mikenskoi, Grosnja, Caucasus.
Fell 1861. Oct. 7, 1½ P. m.	267	91	KLEIN-MENOW, Alt-Strelitz, Mecklen- berg.
		81	Stone. Slab, polished on both sides. Dull brown crust on one end. Fracture looking not unlike brown sandstone. Full of iron grains. [Smith Collection.]
		46	• Rectangular mass, with one polished face, but no crust. [Smith Collection.]
	4.5 2.5 2	* Irregular fragments. [Smith Collection.]  * Two faces cut at right angles. [Smith Collection.]	
Found 1862.	268	140	VICTORIA WEST, Cape Colony, S. Africa.
		143	Iron. Polished slab, with crust on edges, and showing in one part a perfect octahedral cleavage. [Smith Col-
		<b>4</b> 8	lection.]  * Thin slab, etched, showing beautiful fine, and very characteristic, Widmanstättian figures. [Smith Collection.]

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1862.	269	288 47 41 47.5	HOWARD Co., near Kokomo, Indiana, U. S. A.  Iron. Two polished faces, the rest of surface covered with crust. No figures produced by etching. [Smith Collection.]  Thin, polished slab. [Smith Collection.]  * Thin slab, etched. [Smith Collection.]  Irregular piece, with one sawed face. [Smith Collection.]
Found 1862.	270		Botetourt, Virginia, U. S. A.
Found 1862.	271	62 80	SIERRA DE CHACO, ATACAMA DESERT, S. A. Stone. Consisting of olivine and a large amount of iron. One polished face. The rest of surface covered with crust. [Smith Collection.]  * Slab, with crust on edges. [Smith Collection.]
Fell 1862. Oct. 1.	272		SEVILLA, Andalusia, Spain.
Recognized 1862–63.	278		CARLETON IRON, TUCSON, Arisona.
Known before 1863.	274		Wöhler meteorite.
Known 1863.	275	29.5	SOUTHEAST MISSOURI, U. S. A.  Iron. Thin slab, full section, etched, showing very striking Widmanstättian figures covered with innumerable fine Neumann lines and interspersed with masses of bright nickeliferous iron.  [Smith Collection. From St. Louis Acad. of Nat. Science.]  * Slab, similar in every respect to the previous specimen.
Recognized 1863.	276	<b>467</b> 186	SMITH'S MOUNTAIN, ROCKINGHAM Co., Virginia, U. S. A. Iron. One polished face, and the rest of the surface covered with crust.  [Smith Collection.]  The specimen has one broad polished face, the reverse side presenting an appearance as if the iron had been blown

Date of Fall or Find.	No.	Weight in Grams.	Description,
·		88 80	or torn apart, developing a superb octahedral structure, very ragged, but entirely surrounded by a rim of smooth, deeply pitted crust. [Smith Collection.]  Beautifully etched slab, showing typical Widmanstättian figures. Full section. [Smith Collection.]  Like previous specimen. [Smith Collection.]
Found 1863.	277	227	OBERNEIRCHEN, BÜCKEBURG, OLDEN- BERG, Prussia.  Iron. Block, with a black friable crust on two sides, the remaining four faces etched, showing beautiful fine, clear, and perfectly characteristic Wid-
	98	manstättian figures. [Smith Collection.] Rectangular mass, with crust on one face; the other five faces are etched, and cubic plates can be distinguished with those of the octahedron. [Smith Collection.]	
		62 21	Polished slab. [Smith Collection.] Polished slab. [Smith Collection.]
Found 1863.	278	81	DAKOTA, U. S. A.  Iron. Four etched faces, and the rest crust. Some parts show Neumann lines, others very good Widmanstättian plates, and still another face shows no figures whatever. Occasional masses of a bright nickel iron. [Smith Collection.]
Found 1863.	279	1,624 147.5	RUSSEL GULCH, Gilpin Co., Colorado, U. S. A. Iron. Three cut faces, and the rest of the surface showing crust deeply pitted. [Smith Collection.] Slab, etched, showing bent Widmanstättiau plates as seen in Fig. 12, which is printed directly from this slab. [Smith Collection.]
Fell 1863. March 16.	280		PULSORA, RUTLAM, Central India.
Fell 1863. June 2, 7½ a. m.	281		SCHRIKAR STATTAN, BUSCHOFF, Courland, Russia.
Fell 1863. Aug. 8, 12j p. m.	282		AUKOMA, PILLISTFER, Livland, Russia.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1863. August 11.	288	2.5	SHYTAL, 40 miles north of DACCA, India. Stone. Gray, with dull black crust. A polished face shows numerous iron grains. [Smith Collection.]
Fell 1863. Dec. 7, 11 a. m.	284	17	TOURINNES-LA-GROSSE, Tirlemont, Belgium. Stone. Light gray, with dull black crust and one cut face showing iron grains. [Smith Collection.]
Fell 1868. Dec. 22, 9 A. H.	285	10.5	MANBHOOM, Bengal, India. Stone. Light bluish gray, with dull black crust and very little iron. [Smith Collection.]
Found 1863–64.	286	9.5	TOMHANNOCK CREEK, Rensselaer Co., New York, U. S. A. Stone. Thin polished slab, nearly black, and full of iron grains. Shows crust. [In exchange from S. C. H. Bailey.]
Fell 1864. April 12, 43 A. M.	287		NERFT, Courland, Russia.
Fell 1864. May 14, 8 p. m.	288	17 11 1.5 }	ORGUEIL, Tarn-et-Garonne, France. Stone. No iron. Dead black, with white specks, and dull black crust.  [Smith Collection.]  Not so black as previous specimen, but showing well-marked crust. [Smith Collection.]  Specimens showing crust. [Smith Collection.]  Numerous other small fragments, and a quantity of white powder in bottles labelled "Water extract of Orgueil meteorite." [Smith Collection.]
Fell 1864. June 26, 7 a. m.	289	;	Dolgowoli, Volhynia, Russia.
Found before 1865.	290	13.5	COPIAPO, Chili. SIERRA DI DEESA. Iron. Fragment with one etched face, showing Widmanstättian figures very much broken up. [Smith Collection. From the Paris Museum.]
Found 1865.	291		DELLYS, Algiers, Africa.

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1865. Jan. 19.	292	86.5	SUPUHEE, MOUZA KHOORNA, Goruckpur, India.  Stone. Striking breecia-like structure, consisting of light gray angular fragments, of greatly varying size, set in a dark matrix. A polished face shows iron grains distributed through the mass. One portion of the specimen is covered with a smooth dull black crust, while another portion has a thinner crust covered with small pittings. [Smith Collection.]
Fell 1865. March 26, 9 a. m.	293	100.5 48 29 28	Vernon Co., Wisconsin (CLAYWATER), U. S. A.  Stone. Dark brown, full of rusty iron grains, and covered, with the exception of two polished faces, by a dull brown crust. [Smith Collection.]  Thin polished slab, with crust on ends. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]  * Polished slab, but with no well-formed crust. [Smith Collection.]
Fell 1865. May 28, 6 p. m.	294		GOPALPUR, Jessore, India.
Fell 1865. Aug. 12, 7 p. m.	295		DUNDRUM, Tipperary, Ireland.
Fell 1865. Aug. 25, 9 A. M.	296		Umjhiawar, Sherghotty, Berar, India.
Fell 1865. Aug. 25, 11 A. M.	297	20	AUMALE, SENHADJA, Algeria, Africa. Stone. Gray, with one polished face showing some iron. [Smith Collection.]
Fell 1865. Sept. 21, 7 a. m.	298		Muddoor, Mysore, India.
Found 1866.	299 -	88.5	BEAR CREEK, DENVER Co., Colorado, U. S. A. Iron. Etched slab, showing well-marked Widmanstättian figures, also crust, and good octahedral cleavage on edge. [Smith Collection.]
Found 1866.	800		Prambanan, Socrakarta, Java.

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Found 1866.	801	7,519	FRANKFORT, FRANKLIN Co., Kentucky, U. S. A. Iron. Single cleavage octahedron
		'	shown in Fig. 13. [Smith Collection.]
Found 1866.	302		Juncal, Paypote, Chili.
Found 1866.	308	27	BARRANCA BLANCA, San Francisco Pass, Chili.  Iron. Ragged exterior, and two etched surfaces, showing very peculiar figures, surrounding small nodules of troilite. Shown of original size in Fig. 14. [Smith Collection.]
Fell 1866. April.	304	81.5	UDIPI, SOUTH CANARA, India.  * Stone. Gray, with light and dark grains and dull black crust. Two polished faces, showing iron thickly distributed. [Smith Collection.]
		30.5	Similar to previous specimen, only with more crust. [Smith Collection.]  * Also some small fragments.
Fell 1866. May 27.	305		POKHRA, near Bustee, Goruckpur, India.
Fell 1866. May 80, 84 a. m.	306	6	SAINT MESMIM, Troyes, Aube, France. Stone. Fragment, dark and light gray, with smooth dull brown crust and very little iron. [Smith Collection.]
		1	Shows crust. [Smith Collection.]  * Also other small fragments.
Fell 1866. June 9, 5 p. m.	807	533	KNYAHINYA, Unghvár, Hungary. Stone. With one large polished face showing light and dark grains, more or less surrounded with iron. The rest of the specimen is covered by a dull brown crust with small pittings. [Smith Collection. From University of Pesth.]
		256.5	* Similar to previous specimen.  [Smith Collection. From University of Pesth.]
		66	Completely covered with crust.  [Smith Collection. From University of Pesth.]
		29.5	* Similar to previous specimen. [Smith Collection. From University of Pesth.]
Fell 1866. Oct. 5.	<b>30</b> 8		JAMKHEIR, Ahmednuggur, Bombay, India.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1866. Dec. 6.	309	13.5	ELQUERAS, CANGAS DI ONIS, Oviedo, Spain. Stone. Dark gray. One polished face showing breccia-like structure and iron grains. Dull black crust. [Smith Collection.]
Found 1867.	310	52.5	SAN FRANCISCO DEL MESQUITAL, near Durango, Mexico. Iron. Thin slab, with one side etched showing Neumann lines, the other side covered by a smooth crust. [Smith Collection.]
Found 1867.	811		AUBURN, MACON Co., Alabama, U. S. A.
Found 1867.	312		Losttown, Cherokee Co., Georgia, U.S. A.
Fell 1867. Jan. 19, 9 a. m.	313		Кнеткее, Rajpootana, India.
Fell 1867. June 9, 10} P. M.	814	82	TADJERA, Setif, Algiers. Stone. Fragment, black and compact containing articles of what looks like pyrhotite. Smooth black crust. [Smith Collection. Presented by Paris Museum.]
Found 1867.	315	534	ALLEN COUNTY (near Scottsville), Kentucky, U. S. A. Iron. Thin etched slab with crust on all the edges. The etched surface and the inclusions of troilite resemble very closely those of the Coahuila irons. [Purchased from Ward and Howell.]
		21	Slab showing cleavage which appears identical with that of the Saltillo (Sancha estate) iron. [Purchased from Ward and Howell.]
Found 1868.	316	48	GOALPARA, Assam, India. Stone. Curious blue-black mass of irregular grains loosely packed together. Brown woody-looking crust. No iron appearing on polished face. [Smith Collection.]
Fell 1868. Jan. 30, 7 p. m.	817	689	Pultusk, Sielce Nowy, Poland. Stone. Large polished face showing numerous iron grains. Gray color, dull black crust, also showing partially formed crust on recent fracture. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams,	Description.
		110	* Completely covered with crust except on one corner. [Smith Collection.]
		94	Complete individual, but with the crust thinner in some parts than in others. [Smith Collection.]
		94	Crust complete. [Purchased from Liebener Collection.]
	1 1	87	The same.
	1 1	68	The same.
		56.5	Crust complete, except on one edge. [Smith Collection.]
		48.6	Complete, except on one corner. [Purchased from Ward and Howell.]
l		40	Crust complete. [Smith Collection.]
		89	* Crust slightly nicked off. [Smith Collection.]
		37	• Crust slightly nicked off. [Smith Collection.]
		29	* Complete stone. [Purchased of Ward and Howell.]
		25.5	* Complete stone. [Smith Collection.]
		7.5 8	* The same. * The same.
		7	* Fragments with crust. [Smith Col-
		6.5 5.5	lection.]
Fell 1868. Feb. 29, 11 A. M.	318		MOTTA DI CONTI, CASALE, Piedmont.
Fell 1868. Mar. 20.	819		Daniel's Kuil, Griqualand, South Africa.
		22	Stone. Fragment. Dark gray, fine grained, with particles of iron through the mass. [Smith Collection.]
Fell 1868. May 22, 10} A. M.	320		SLAVETIC, Agram, Croatia.
Fell 1868. June 20-30, 8 p. m.	821		PNOMPEHN, Cambodia, India.
Fell 1868. July 11.	322	2.5	ORNANS, Doubs, France. Stone. Fragment looking like a bluish gray clay or hardened mud.
		1	Almost no iron. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]
Fell 1868. Sept. 8, 24 A. M.	323	6	SAUQUIS, St. Etienne, Basses-Pyrénées, France. Stone. Fragment, light gray with silvery grains of iron. [Smith Collection. Gift of Paris Museum.]

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1868. Oct. 1.	324		Lodran, Mooltan, India.
Fell 1868. Nov. 27, 5 p. m.	325	84	DANVILLE, Alabama, U. S. A. Stone. Irregular fragment, gray color, and dark brown crust. The en- tire mass is intersected by a network of dark gray veins, and grains of iron
[ ]		15.5	sprinkled through. [Smith Collection.]  * Similar to previous specimen, only
		5.5	without crust. [Smith Collection.]  * Shows crust. [Smith Collection.]  Also some fine powder.
Fell 1868. Dec. 5.	326	106	FRANKFORT, FRANKLIN Co., Alabama, U. S. A. Stone. Gray, with very little iron showing on polished face. Grains of all colors, notably dark ones. Black vitreous crust with raised veins like the
		21	markings left by the palm of the hand on an oily surface. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]
Fell 1868. Dec. 22.	827	7.5	MOTEREA NUGLA, BHURTPUR, India. Stone. Dark gray slab, polished on both sides, full of iron grains. Crust on one end. [Smith Collection.]
Found 1869.	828		UTAH (between Salt Lake City and Echo), U. S. A.
Found 1869.	329		SHINGLE SPRINGS, Eldorado Co., California, U. S. A.
Fell 1869. Jan. 1, 121 r. m.	330	868	HESSLE, near Upsala, Sweden. Stone. Completely covered with a dull black crust, except on one corner where it shows a gray fracture, with iron grains sprinkled through the mass.  [Smith Collection. From Royal Museum, North Collection.]
		59	Stockholm.] Completely covered by
		66	crust.  * Fragment half covered with crust.  [Smith Collection. From
		37 9.5 5.5	* Complete individual.  * Shows crust.  * One polished face and crust.  * Complete individual.  * Royal  * Museum,  * Stockholm.]

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Date of Fall or Find.	No.	Weight in Grams.	Description.
		2 1.5 .6 .4	* Crust complete.  * From Royal Museum, Stockholm.  * Other small fragments. [Purchased from Ward and Howell.]
Fell 1869. May 5, 64 p. m.	831		Krähenberg, Zweibrücken, Bavaria.
Fell 1869. May 22, 10 p. m.	<b>3</b> 32	865	KERNOUVE, CLEQUEREC, Morbihan, France. Stone. Gray, fine-grained, compact, with dull brown crust. One cut face showing grains of iron. [Smith Collection. From F. Psaini.]
		41	* Irregular fragment. [Smith Collection. From F. Psaini.]
Fell 1869. Sept. 19, 9 p. m.	333		Тјави, Pandanjan, Java.
Fell 1869. Oct. 6, 113 a. m.	834	46	LUMPKIN, STEWART Co., Georgia, U.S. A. Stone. Gray, with darker grains and dull black crust. One face polished, showing iron grains. [Smith Collec- tion.] Thin polished slab, with crust on
		4 2 1.5 1.5 .5	edges. [Smith Collection.]  * Similar to previous specimen. [Smith Collection.]
Fell 1870. Jan. 28.	335	20.5	NEDAGOLLA, Mirangi, Vizagapatam, India.  Iron. Slab, with one face etched, showing only a mottled surface. [Smith Collection.]
Fell 1870. June 17, 2 p. m.	836		IBBENBUHREN, Westphalia, Prussia.
Fell 1870. Aug. 18.	337		CABEZZO DE MAYO, Murcia, Spain.
Described 1871.	338		IQUIQUE, Peru.
Found 1871.	889		Oczeretna, Lipovitz, Kiev, Russia.
Fell 1871. Spring.	340		Roda, near Huesca, Aragonia, Spain.

Date of Fall or Find,	No.	Weight in Grams.	Description.
Fell 1871. May 21, 8½ a. m.	341	20 10.5	SEARSMONT, Waldo Co., Maine, U.S.A. Stone. Light gray, with darker grains and fine specks of iron. [Smith Collection.] Fragment showing a dull black crust. [Smith Collection.] Also numerous small bits, of less than a gram each. [Smith Collection.]
Fell 1871. Dec. 10, 14 p. m.	342		Bandong, Goemoroeh, Java.
Found 1872.	843		Nenntmannsdorf, Pirna, Saxony.
Found 1872.	344	1,675	WACONDA, Mitchell Co., Kansas, U. S. A. Stone. Light gray, friable clay- like mass, containing very little iron. Partly covered by a dull black crust. [Smith Collection.]
		516.5	Similar to previous specimen. [Smith Collection.]
		364	Similar to previous specimen. [Smith Collection.]
		867	Fragment without crust. [Smith Collection.]
		51.5	Fragment showing crust. [Smith Collection.]
		8	Fragment without crust. [Smith Collection.]
		275	Small fragments from five grams down, many of them showing the crust. [Smith Collection.]
Fell 1872. May 8.	345		DYALPUR, Sultanpur, Oude, India.
Fell 1872. June 28, Noon.	346		SIKKENSAARE, TENNASILM, Esthland, Russia.
Fell 1872. July 28, 5½ p. m.	347		Lancé, Authon, Orléans, France.
Fell 1872. Aug. 81, 51 a. m.	348		ORVINIO, near Rome, Italy.
Found 1873.	349	103	CHULAFINNEE, CLEBURNE Co., Alabama, U. S. A. Iron. Highly polished slab, with crust on edges. [Smith Collection. From A. Otto.]
		56	* Etched slab, showing well-marked Widmanstättian figures. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams,	Description.
Found 1873.	350		Ssyromoltow, Angara, Siberia.
Recognized 1878.	351	222	DUEL HILL, Madison Co., North Carolina, U. S. A.  Iron. A large etched face shows curious Widmanstättian figures. In some parts good octahedral plates with inclusions of bright nickel-iron, but other portions of the surface are cracked up into irregular grains, showing no evidence of Widmanstättian plates. The exterior shows a well-marked octahedral classes.
		21.5 3	dral cleavage. [Smith Collection.]  * Fragment with etched surface, and marked octahedral cleavage on exterior. [Smith Collection.]  * Irregular fragment. [Smith Collection.]
Fell 1873. June.	352	53	JHUNG, Punjaub, India.  Stone. Dark gray, full of darker grains. Three polished faces show considerable iron. On two sides covered with a black spongy crust. [Smith Collection.]
Fell 1873. Sept. 23, 5 a.m.	853	69	KHAIRPUR, Mooltan, India. Stone. Dark-colored, compact, and full of fine iron particles. Nearly covered by a thin black crust, excepting two polished faces. [Smith Collection.]
Found 1874.	354	8,028	BUTLER, BATES Co., Missouri, U. S. A. Iron. Mass, with two sawed faces at right angles to each other, and the rest crust. [Smith Collection.]
		2,919	One large polished surface, with one half of it etched, showing beautiful Widmanstättian figures. Contains two large nodules of troilite. The rest crust. [Purchased.]
		1,439	Mass with crust, and three etched faces cut at right angles to each other, in one of which is a large nodule of troilite. On one corner an octahedral cleavage appears, showing that one of the etched faces is parallel to an octahedral plane. Fig. 15 shows a sketch of this etched face somewhat roughly reproduced so that the finest lines do not appear. On the original specimen

Date of Fall or Find.	No.	Weight in Grams.	Description.
		1,185 388 326 } 282 }	there is every gradation between coarse, typical Widmanstättian figures and the finest microscopic markings. [Smith Collection.]  A cleavage octahedron broken out of the previous specimen. All the faces were perfectly smooth except part of one which was hollowed out by coming in contact with the crust. One etched face of this octahedron is shown in Fig. 15. By following the Widmanstättian figures on to adjacent faces of the octahedron, it was found that nearly all, including the finest microscopic markings, were due to plates parallel to octahedral faces, the only exception being the markings seen in the diagram perpendicular to the octahedral edges, and these proved to be due to plates parallel to a face of the rhombic dodecahedron.  Three polished faces at right angles, and the rest of the surface covered with crust. [Smith Collection.]  Beautifully etched slab with a nodule of troilite in the middle of it, and the crust on one end. [Smith Collection.]  Similar to previous specimen.  [Smith Collection.]  Also a two gram nodule of troilite
Found 1874.	855	275.5 173.5 167 87.5	MEJILLONES, near DESERT OF ATACAMA, South America.  Belonging to the Pallas group, but very fine-grained. The specimen shows a crust, and on three polished faces the iron appears very unequally distributed, usually in small grains hardly forming a continuous network, but occasionally large masses of iron appear.  [Purchased of Ward and Howell.]  Three polished faces; also shows crust and fracture. [Smith Collection.]  Similar to previous specimen.  [Smith Collection.]  Five cut faces, and shows crust and fracture. [Smith Collection.]
Fell 1874. May 11, 11} p. m.	856		SEVRUKOVO, near Brlgorod, Kursk, Russia.

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1874. May 14, 24 r. m.	857	211 28.5 6 6 4	Nash County, near Castalia, North Carolina, U. S. A.  Stone. One half dark gray full of light-colored grains, the other half nearly white with only occasional grains of dark gray, the light and dark halves of the specimen being divided by a sharp line at the plane of contact. Iron grains are scattered through the mass, and a large part of the specimen is covered with a smooth slightly porous dark brown crust [Smith Collection.]  * Fragment of the darker portion. [Smith Collection.]  * The same, showing crust. [Smith Collection.]
		1.5	Numerous other small fragments.
Fell 1874. May 20.	358		VIRBA, Viddin, Turkey.
Fell 1874. Nov. 26, 104 a. m.	359		KERILIS, MAEL PESTIVIEN, Côtes-du- Nord, France.
Known 1875.	360	917  484 219.5  279  131  141.5  114 94.5  74.5 45.5 33.0 81.5 88.5	Santa Catarina, Rio San Francisco do Sul, Brazil.  Iron. Partly dark colored, but the greater portion of a light bronze, and having apparently a very marked cubic cleavage. [Smith Collection.]  * Mostly crust. [Smith Collection.]  * Entirely crust, looking like limonite. [Smith Collection.]  * Iron, with very imperfect Widmanstättian figures on etched surface. [Smith Collection.]  * Apparently crust. [Smith Collection.]  Partly crust, and partly iron. [Smith Collection.]  * Mostly crust. [Smith Collection.]  * Iron, with cubic cleavage. [Smith Collection.]  * Mostly iron, with cubic cleavage. [Smith Collection.]  * Mostly iron, with cubic cleavage. [Smith Collection.]  Green and yellow porous mass, looking like slag. [Smith Collection.]

	1_	Weight	
Date of Fall or Find.	No.	in Grams.	Description.
		50 } 18.5 }	Similar to previous specimen. [Smith Collection.]
		215	, In fragments of all sorts. [Smith Collection.]
·	İ		This iron is regarded by some as be-
j			ing of terrestrial origin, but the above specimens appear to be meteoric.
Fell 1875. Feb. 12, 10; p. m.	361		Homestead, West Liberty, Iowa Co., Iowa, U. S. A.
		5,425	Stone. Fragment, dull gray, with iron grains sprinkled through the mass.
			Nearly covered with a dull black
			crust, deeply pitted. [Smith Collection.]
		2,803	Complete individual, covered entirely with crust. [Smith Collection.]
		1,746	Fragment, with crust.   Smith
		1,691	Complete individual. > Collection 1
		1,677	* Complete individual. J Cometton. J Individual, completely covered with
	l	1,346	crust, except that on one side the crust
			is only thinly formed over a surface of
			recent fracture. [Smith Collection.]
		875	* Complete individual. [Purchased of Ward and Howell.]
		685	* Complete individual, but with sur-
			faces showing imperfectly formed crust. [Smith Collection.]
		286	* Fragment, showing crust, also crust partially formed over fracture.
			[Smith Collection.]
		278	* Fragment, showing crust. [Smith Collection.]
		200	One polished face, elsewhere crust.
		139	[Purchased of Ward and Howell.]  * Complete individual, with coatings
			of different thicknesses. [Smith Collection.]
		63	* Irregular fragment.
		74	* Fragment, with crust.
		51	Fragment, with crust. [Smith
		21 80	• Fragment, with crust. [Collection.] • No crust.
		4	* No crust.
Fell 1875.	362		SITATHALI, southeast of Raepur, Central
March 4.		1,	Provinces, India.
		14	Stone. Polished slab, dark gray, with iron grains, and dull black crust
			on one end. [Smith Collection.]

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1875. March 81.	863		ZSADANY, Temeser Banat, Hungary.
Fell 1875. April 24.	364		NAGERIA, Fathabad, India.
Fell 1875. August 16, Noon.	865		FEID CHAIR, LA CALLE, Algeria.
Found 1876.	366		VERKHNE-DNIEPROVSK, Ekaterinoslav, Siberia.
Fell 1876. Feb. 16.	367		JUDESEGERI, Kadaba Taluk, Mysore, India.
Fell 1876. April 20, 84 p. m.	368	17	Rowton, near Wellington, Shropshire, England.  Iron. Etched slab, showing good Widmanstattian figures, and a smooth bluish black crust on edge. [Smith Collection.]
Fell 1876. June 19.	369		VAVILOVKA, Kherson, Russia.
Fell 1876. June 28, 11} A. M.	870		STÄLLDALEN, Nya Kopparberg, Sweden.
Fell 1876. Dec. 21, 83 p. m.	371	75	ROCHESTER, FULTON Co., Indiana, U.S.A. Stone. Light gray fragment with darker grains and spongy dark brown crust. Very little iron. [Smith Collection.]
Found 1877.	<b>87</b> 2	202 183 54 86.5	Dalton, Whitfield Co., Georgia, U. S. A. Iron. Block, with two cut faces at right angles, elsewhere crust. [Smith Collection.] Full section slab, etched, showing very striking and characteristic Widmanstättian figures.  * Etched slab. Crust on edge. [Smith Collection.]  * Etched slab. Crust on edge. [Smith Collection.]
Found 1877.	<b>37</b> 3	107 68 49	CASRY COUNTY, Georgia, U. S. A.  Iron. One etched face, showing broad but somewhat cracked-up Widmanstattian figures, elsewhere crust.  [Smith Collection.]  Piece forged into the shape of a coldchisel. [Smith Collection.]  * Full section etched slab. [Smith
			Collection.]

			<del> </del>
Date of Fall or Find.	No.	Weight in Grams,	Description.
		65	• Irregular mass, showing octahedral cleavage. [Smith Collection.]
Found 1877.	374		MANTOS BLANCOS (Cerro Hicks), DESERT OF ATACAMA, South America.
Found 1877.	375		SERRANIA DE VARAS, DESERT OF ATA- CAMA, South America.
Fell 1877. Jan. 8.	376	242	WARRENTON, WARREN Co., Missouri, U. S. A. Stone. Bluish gray, soft, clay-like mass, with very little iron, and a char-
Fell 1877. Jan. 23, 4 p. m.	377	166 74 28 16.5 45 8,113 539 424.5 6.5 6 2 1.5 1	acteristic porous or spongey blue-black crust. [Smith Collection.]  Similar to previous specimen. [Smith Collection.]  Fragment without crust [Smith Collection.]  Fragment showing crust. [Smith Collection.]  Similar to previous specimen, only that it has clinging to it some of the woody fibre of the tree which the meteorite struck in its fall. [Smith Collection.]  In fragments varying in size from one to six grams, and most of them showing crust. [Smith Collection.]  CYNTHIANA, HARRISON CO., Kentucky, U.S. A.  Stone. Dull gray, with white grains and some iron. This specimen shows a distinct front, consisting of a nearly flat surface, covered with a dull black crust full of small round pittings. This crust has flowed back in deep furrows piling up into a point behind. Quite a large piece has been broken from one edge of the specimen. [Smith Collection.]  Fragment of the above specimen, showing crust.  Fragment with crust.  Fragment without crust.
			Other small olds.

YOL XXIII. (N. S. XIV.)

Date of Fall or Find.	No.	Weight in Grams.	Description.
Fell 1877. May 17.	378		Hungen, Hesse, Germany.
Fell 1877. June.	379		CRONSTADT, Orange River, Free State, South Africa.
Fell 1877. Oct. 18, 2 p. m.	380	196.5 60	SARBANOVAC, SOKO-BANJA, Alexinatz, Servia. Stone. Light gray fragment, with large dark gray grains, and some iron particles. Partly covered with a dark-brown pitted crust. [Smith Collection. From J. R. Gregory.]  One polished face, also crust. [Smith Collection.]
Fell 1878. June 11, 11; A. M.	381		LA CHARCA, Irapuato, Mexico, U. S. A.
Fell 1878. July 15, 13 p. m.	882	10.5	TIESCHITZ, Prerau, Moravia. Stone. Dark gray, with numerous lighter grains, and smooth dull black crust. [Smith Collection.]
		7.5	* Same, but with one face polished, showing very little iron. [Smith Collection.]
Fell 1878. Sept. 5.	383		DANDAPUR, Goruckpur, India.
Fell 1878. Nov. 8.	384		RAKOVKA, Tula, Russia.
Fell 1878. Nov. 27, 6 p. m.	385		DHULIA, Khandeish, India.
Found 1879.	386		CAMPO DEL PUCARA, Catamarca, Argentina, South America.
Found 1876.	387		GREEN COUNTY, Tennessee, U. S. A.
Found 1879.	388	6	LICK CREEK, Davidson Co., North Carolina, U. S. A.  Iron. Irregular fragment, showing no Widmanstattian figures on the polished surface, but might on a different section. [Smith Collection.]
Fell 1879. Jan 81	389		LA BÉCASSE, Dun-le-Poëlier, Inde, France.
Fell 1879. May 10, 5 p. m.	390	12,605	ESTHERVILLE, EMMET Co., Iowa, U.S. A.  ("The Perry Meteor.")  Iron. Consisting of a network of

Date of Fall or Find.	No.	Weight in Grams.	Description.
		1,001.5 821 595.5 492 489 481 162 148 103 83.5 61.5 61.5 50 46 17 297	iron enclosing olivine, but the proportion of the two varying largely in different parts of the meteorite. This specimen is a ragged mass partially covered with a bluish-black crust deeply pitted. It also contains a nodule of transparent cleavable olivine 8 cm. in diameter. [Purchased.]  One face polished, showing on the iron Widmanstättian figures before being etched.  Similar to previous specimen, but mostly iron.  Mass looking like slag, but showing the iron network on a cut face.  Individual, containing small amount of iron and completely covered with crust.  Individual, mostly iron.  Stony-looking mass.  Pure iron, showing beautiful Widmanstättian figures.  Individual, mostly iron.  """"  Stony-looking mass.  Similar, but with one cut face.  One polished face.  Nodular masses from 50 grams down to fine grains. 208 specimens, all individuals, and nearly pure iron.  Of the stony portion in fragments.
Fell 1879. May 17, 4 p. m.	391		Gnadenfrei (Schobergrund), Silesia, Germany.
Fell 1879. Aug. 1, Evening.	392		NAGAYA, Entre Rios, Argentina, South America.
Fell 1879. Nov. 4.	893		Kalumbi, Saltara, India.
Fell 1880.	394	90	AUSTRALIA.  Iron. This specimen is labelled in the collection of J. L. Smith, as given above, with the date 1880. It appears to be a complete individual, and belongs to the Pallas group, consisting of a network of iron enclosing grains of olivine.

Date of Fall or Find.	No.	Weight in Grams,	Description.
Found 1880.	395		IVANPAH, SAN BERNARDINO Co., California, U. S. A.
Found 1880.	396		LEXINGTON COUNTY, South Carolina, U. S. A.
Found 1880.	397		CARROL COUNTY, Kentucky, U. S. A.
Fell 1880. Feb. 18, 5} A. M.	398		Toke uchi mura, or Tajima, Yofugori, Japan.
Fell 1880. May.	399	11.5	KARAND, VERAMIN, Teheran, Persia. Stone. Contains olivine. Dull brown crust. Polished face shows considerable iron.
Fell 1881. Mar. 14, 8} P. M.	400		Pennyman's Siding, Middlesborough, England.
Fell 1881. Nov. 19, 6} a. m.	<b>4</b> 01		GROSS-LIEBENTHAL, near Odessa, Russia.
Found 1882.	402	31.5	JENNY'S CRREE, WAYNE COUNTY, West Virginia, U. S. A. Iron. Fragment, with one face polished and etched, showing coarse Widmanstättian figures. Also shows wellmarked octahedral cleavage. [In exchange from S. C. H. Bailey.]
Found 1882.	403		HEX RIVER MOUNTAINS, CAPE COLONY, South Africa.
Found 1882.	404		ALEXANDER COUNTY, North Carolina, U. S. A.
Found 1882.	405		GREENBRIER COUNTY, Alleghany Mts., West Virginia, U. S. A.
Fell 1882. Feb. 8, 4 p. m.	406	910	Mócs, Kolos, Transylvania. Stone. Completely covered with a dull brown crust of three different thicknesses. [Purchased in Vienna soon
		350	Has one polished face, showing light gray color and rusty iron grains. The rest of the surface is covered by the crust. [Purchased in Vienna soon after
-		89.5	fall.]  * Similar to previous specimen. [Purchased in Vienna soon after fall.]

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Date of Fall or Find.	No.	Weight in Grams,	Description.
Found 1882. June 10. Fell 1882.	407	40 11	* Completely covered by crust. [Purchased in Vienna soon after fall.]  Covered with crust, excepting one polished face, which is intersected by very heavy cracks filled with fused crust. [Purchased in Vienna soon after fall.]  MAVERICK COUNTY, Texas, U. S. A.  PAYLOVKA, Karai, Balaschev, Russia.
Aug. 2, 44 P. M. Found 1883.	409	56.5	GRAND RAPIDS, Michigan, U. S. A. Iron. Polished slab, showing crust. One face etched, exhibiting very striking Widmanstättian figures, made of thin plates packed together in bundles. [In exchange from the U. S. National Museum.]
Found 1883.	410		Adalia, Konia, Asia Minor, Turkey.
Fell 1883. Jan. 28, 23 P. M.	411		SAINT CAPRAIS-DE-QUINÇAC, Gironde, France.
Fell 1883. Feb. 16, 8 p. m.	412	738	ALFIANELLO, Brescia, Italy. Stone. Gray fragment, sprinkled through with iron grains, and partially covered with a brown crust deeply furrowed.
·Fell 1883.	413		Ngawi, Djogorogo, Java.
Found 1884. May.	414	546 367	GLORIETA MOUNTAIN, near Canoncito, Santa Fé County, New Mexico.  Iron. Etched slab, showing typical Widmanstättian figures. Deeply pitted crust on edges. [In exchange from George F. Kunz.]  Etched slab, with crust on edges. [Purchased from Eimer and Amend.]
Found 1884. June.	415		INDEPENDENCE COUNTY (Joe Wright Mountain), Arkansas, U. S. A.
Found 1885.	416		Catorze, near San Luis Potosi, Mexico.
Fell 1885. Nov. 27, 9 p. m.	417		MAZAPIL, Zacatecas, Mexico.
Fell 1886. March 27, 8 p. m.	418		CABIN CREEK, JOHNSON COUNTY, Arkansas, U. S. A.

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Date of Fall or Find.	No.	Weight in Grams.	Description.
Described 1887.	419	9.3	ABERT IRON.  Iron. Thin etched slab, showing well-marked Widmanstättian figures.  [In exchange from U. S. National Museum.]
Found 1887.	<b>42</b> 0	114	EAU CLAIRE, Wisconsin.  Iron. Etched slab with crust on edges, showing well-marked octahedral structure. [Presented by Davenport Fisher, Esq., of Milwaukee.]
Described 1887. May 80.	421		POWDER MILL CREEK, Crab Orchard, Cumberland Co., Tenn., U. S. A.
Described 1887. August 26.		670	Rockwood, Cumberland Co., Tenn.  Large polished section, with deeply pitted crust, showing grains of iron in an earthy matrix said to consist of enstatite and anorthite. Same as Powder Mill Creek. [Purchased from Ward and Howell.]
Described 1887. May 30.	422	12.5	Waldron's Ridge, Tazewell Co., Tennessee, U. S. A. Iron. Fragment of crust. A part shows an octahedral structure, the plates being separated by a thin foil of nickeliferous iron, resembling the specimens from Cocke Co. [In exchange from G. F. Kunz.]
Described 1887.	423	27	CHATTOGGA COUNTY, Georgia, U. S. A.  Iron. Fragment with two polished faces, and showing crust. Dilute acid at first blackens the surface slightly, and by continued action develops fine Neumann lines similar to those exhibited by the Coahuila irons. It also resembles the Coahuila irons in being easily cut by a knife. It contains large inclusions of troilite altered by weathering. [In exchange from G. F. Kunz.]
Fell 1887. Jan. 21.	424		TALBOT ROAD, De Cewsville, Ontario.

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SIERRA DE CHACO	82	271	Тјаве	. 90	888
SIERRA DI DEESA	84	290	TOCAVITA	. 49	61
Sigena	44	19	TOKE UCHI MURA	. 100	898
SIGNET-IRON	70	198	TOLUCA	. 44	22
SK1	69	188	Tomhannock Creek	. 84	286
SIKKENSAARB	91	846	TOULOUSE	. 50	66
Simbirsk	60	`188	Tounkin	. 58	96
SIMONOD	57	126	Tourinnes-La-Grosse .	. 84	284
SIRATIK	43	15	TRENTON	. 78	248
SITATHALI	95	862	Trenzano	. 76	281
SLAVETIC	88	<b>820</b>	Tucson (Sonora)	. 70	193
SLOBODKA (Partsch)	60	184	Tucson (Carleton Iron) .	. 82	278
SLOBODKA (Smolensk)	<b>52</b>	81	TUCUMAN	. 44	20
SMITH COUNTY	62	144	TULA	. 67	172
SMITHLAND	65	148	Tunja	. 49	59
Smith's Mountain	82	276			
Smolensk (Kikino)	49	57	Uden	. 65	151
Smolensk (Slobodka)	<b>52</b>	81	Udipi	. 86	804
Smolensk (Timoschin)	47	50	Umballa	. 53	92
SOCRAKARTA	85	300	Umjhiawar	. 85	296
Soko-Banja	98	880	Union County	. 72	204
Sonora	70	193	UTAH	. 89	828
SOUTH CANARA	86	304	UTRECHT	. 66	160
Southeast Missouri	82	275			
SSTROMOLTOW	92	350	<b>V</b> <sub>A</sub> GO	. 43	7
STAARTJE	65	151		. 96	<b>36</b> 9
Ställdalen	96	870	VERAMIN	. 100	399
STANNERN		55	Veresegyháza	. 77	288
STAUNTON	77	242	VERKHNE-DNIEPROVSK .	. 96	866
STAVROPOL	77	284		. 67	168
STEINBACH	41	8		. 74	213
STEWART COUNTY	90	334	VERNON COUNTY	. 85	293
STINKING CREEK	73	205		. 48	7
SUPUHER	85	292		. 81	268
SZLANICZA	65	147		. 94	358
			VOLHYNIA (Okniny)	. 56	120
_				. 52	79
TABARZ	74	215	Vouillé	. 55	114
TABOR		13	***		
TADJERA	87	314		. 91	844
	100	398		. 102	422
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W1TME88	45	25	ZACATECAS 4	28
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#### VI.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF THE MUSEUM OF HARVARD UNIVERSITY.

# VIL — ON THE STRUCTURE OF THE FROND IN CHAMPIA PARVULA, HARV.

#### BY ROBERT PAYNE BIGELOW.

#### Presented June 16, 1887.

THERE is a small group of the Florideæ, consisting of the genera Chylocladia, Lomentaria, and Champia, that is of particular interest from the entirely anomalous condition of the frond. The frond is hollow, is generally chambered, has thin walls, and contains peculiar filaments running longitudinally close to the inner wall. Of this group, Champia parvula and Lomentaria Baileyana are abundant along the New England coast south of Cape Cod. The former species being the more convenient, was selected from a study which I began in November last at the suggestion of my instructor Dr. W. G. Farlow.

In order to understand the points at issue, it is first necessary for us to get a general idea of the structure of the plant that we are studying. In general aspect the frond of *Champia parvula* is jointed, cylindrical, and much branched; forming a tuft four to six centimeters high. The branches are given off at the joints, or constrictions; either singly, or else in pairs, or whorled (Plate, Fig. 1). If a portion of the frond be cut open lengthwise and examined with a low power of the microscope, it will be seen to be chambered, the barrel-shaped chambers being separated by cellular diaphragms and becoming progressively smaller towards the apex (Figs. 1, 2). The diaphragms are always at the joints or constrictions above referred to.

A little more careful attention will reveal a number of straight filaments (Fig. 2, f) running from the base of a branch to its tip, where they converge. As far as my observations go, the number of filaments in a branch may vary from eleven to fifteen. It will be noticed that all the filaments in each chamber have projecting from

their inner side one or two little globular or pear-shaped cells (Diagram, B). Bulb-cells we might call these for want of a better name. With a little higher power than is necessary for making out these

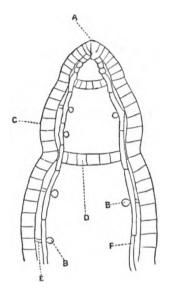


DIAGRAM OF A LONGITUDINAL SECTION OF A TIP OF C. PARVULA.

A, the apex; B, bulb-cell; C, cortex; D, diaphragm; E, connection between filament and cortex; F, filament.

points, one may observe that each filament is composed of a single row of long cylindrical cells united by their ends. There are three or four of these cells to a chamber. The bulb-cell is always in the neighborhood of the middle of the filament cell to which it is attached; and opposite to it, that is, on the outer side, the filament is usually connected with the cortex, often by means of a short slender cell. The filaments pass through the diaphragms practically unchanged. Usually it is the middle part of the penetrating filament cell that is in immediate contact with the diaphragm, and the ends of two filament cells never meet in the plane of the diaphragm. Moreover, this filament cell that penetrates the diaphragm never bears a bulb-cell, as far as I have seen. I can discover no direct connection between the filaments of one branch and those in the rest of the plant. They merely converge into a small space at the base of the branch opposite the diaphragm of the main stem, and there they end.

The wall of the frond, or cortex, and the diaphragms, are each composed of a single layer of cells very similar in size and shape. In shape these cells are somewhat flattened on their free sides, while those portions in contact are polygonal. Of the three dimensions of the cell, the one at right angles to the layer is the shortest in the adult cells of both the diaphragms and the cortex. In the older cells of the cortex the longitudinal diameter tends to become the longest. Towards the tip of the plant, the radial diameter of the cells of the cortical layer does not decrease much until very near the apex, but the other two diameters decrease more rapidly, so that the cells become columnar (Fig. 2). The whole plant is covered with an apparently gelatinous cuticle, and the chambers contain what appears from alcoholic material to be a viscid fluid. It becomes hardened in alcohol, and is easily stained.

All this is by way of introduction to a more careful examination of the tip of the plant, which it will be necessary to make in order to see just how growth takes place there, and to discover, if we can, how the cells of the cortex and of the longitudinal filaments arise, and what is the origin of the bulb-cells and of the diaphragms. The material that I used in my attempt to answer these questions was collected by Dr. Farlow at Wood's Holl, and preserved in moderately strong alcohol. From the smallness and delicacy of the object to be studied, and the consequent difficulty of making free-hand sections, it was evident that nothing more was to be discovered by that means than what I have already described. I therefore attempted to apply the methods now in use by all animal histologists, of imbedding in paraffine and sectioning with the microtome into ribbons. As the tissues of this plant contain larger cavities with comparatively very thin walls my chief difficulty was to get this tissue into the paraffine without allowing it to collapse. Another difficulty was that when I stained with aniline colors they would become washed out during the subsequent manipulation.

Both difficulties were avoided quite successfully in the following manner. My material was put into 70% alcohol. From this, portions that I wished to section were transferred to 90% alcohol to harden. After being hardened, the specimen was stained. If it was to be stained with some coal-tar color, I used a very strong solution in 90% alcohol. If I wanted to get a hæmatoxylin stain, I transferred the specimen back to 70% alcohol and used Klemenberg's method, or, more frequently, this method with the calcium chloride omitted. After remaining in the stain about forty-eight hours, if the vol. XXIII. (N. 8 XV.)

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stain was hæmatoxylin, the specimen was partly decolorized in the usual manner with very dilute hydrochloric acid in 70% alcohol; if the stain was some aniline, the surplus stain was simply washed out in the 90% alcohol into which the specimen was always put next. From 90% alcohol it was transferred to absolute alcohol, then allowed to sink through alsolute alcohol into chloroform, then put into pure chloroform. I then used a slight modification of the familiar chloroform method of imbedding in paraffine. I employed three mixtures of soft paraffine and chloroform. No. 1 was a saturated solution; No. 2 was two volumes of No. 1 plus one volume of chloroform; No. 3 was one volume of No. 1 plus two volumes of chloroform. The preparation was passed from pure chloroform into No. 3, into No. 2, and then into No. 1. After the preparation was thoroughly saturated with solution No. 1, the vial was uncorked and warmed until the chloroform was all evaporated, or very nearly so. After this the specimen was put into the soft paraffine bath, from this into the hard paraffine, and then imbedded, sectioned in ribbons, and mounted with Schällibaum's fixative and benzole balsam in the usual way.

In staining I obtained the best results with hæmatoxylin. It brings out the cell walls and nuclei well. Eosin shows the protoplasmic contents of the cells better, but leaves the boundaries indistinct. I obtained fair results with methyl-violet and safranin.

It may be well before proceeding farther to examine the literature that has already appeared bearing on our subject. The first publication of interest in this connection is by Carl Nägeli. In "Die Neuern Algensystem," (Zurich, F. Schulthess, 1847, p. 246,) he treats of the structure of Lomentaria kaliformis and of its method of growth. After describing the thallus as hollow, jointed, and with whorled branches, the joints being separated by cellular diaphragms, he goes on to say that at the tip of the branch there is an apical cell (Scheitelzelle) which he supposes to divide by oblique partitions. He does not seem to have made this out very clearly, however. He says that the wall of the thallus is two-layered, and he points out that in the younger portion each of the outer cells abuts against a smaller inner cell. cells divide perpendicularly to the thallus, each into three or more, and thus the cortex is formed; while the inner cells do not divide, but become extended longitudinally and form the longitudinal filaments. Nägeli finds fifteen of these filaments in the adult frond. Their component cells are so elongated that it only takes two of them to reach the length of a joint. Upon the inner side of each of these cells near its middle there is a small globular or pear-shaped cell, or sometimes

two or three of them whorled. He says they seemed to be formed by an outgrowth from the long cell.

A paper appeared in 1882\* by Dr. G. Berthold, in which he incidentally gives a general description of structure and method of growth in *Champia parvula*, *Lomentaria kaliformis*, *Chylochladia reflexa*, Harv., and *Ch. mediterranea*, J. Ag.

He gives a diagram of the tip of Champia parvula, and points out that there is not a single apical cell, but a group of them, and according to him they are arranged in a very definite way. At the apex four of these cells form a cross, only two of them however meeting in the middle. From the outer side of each of these cells is given off a row of cells derived from this apical cell, and very gradually In the angles of the cross thus formed are increasing in width. four other apical cells which give rise to similar rows; and then the remaining space is filled by a third series, usually of eight apical cells and their progeny, making in all sixteen rows of cells each headed by an apical cell. The cells of these rows are flattened at right angles to the axis, and give rise to other cells by oblique division. According to Berthold, these second cells may divide again in like manner, thus forming the peripheral covering cells, while the first do not divide, but become much enlarged.

Berthold was the first to point out that the longitudinal filaments of the adult frond correspond exactly in number and position to the apical cells in *Champia*.

In 1886, in a paper by N. Wille,† we again come across a study of Lomentaria kaliformis. He finds in this species a conical apical cell, which, dividing in several directions, sometimes parallel to its base, sometimes at right angles to the surface of the thallus, gives rise to other cells. These cells again divide into an inner small cell and an outer large one, the outer one dividing again into two. The outer cells are the only ones in which division continues. The inner ones do not divide, but, elongating, produce the longitudinal filaments. Wille hints that the diaphragms are derived from these filaments, but he does not tell how.

Summing this up, we see that Nägeli thinks there is a single apical cell in *Lomentaria kaliformis*; and Wille describes one very clearly



Berthold, Dr. G., Beiträge zur Morphologie und Physiologie der Meersalgen. Jahrbücher f. wiss. Botanik, Bd. XIII., 1882, p. 686.

<sup>†</sup> Wille, N., Beiträge zur Entwickelungsgeschichte der physiol. Gewebesysteme bei einigen Algengattungen. Bot. Centralblatt, 1886, VII., Qr. XXVI. p. 86.

for this species, but does not figure it. On the other hand, Berthold finds a cluster of apical cells in the tip of *Champia parvula*, of which he gives a diagram. The only thing bearing on the other problems suggested by our preliminary examination of *Champia* is Wille's hint that the diaphragms are derived from the filaments.

My observations on the apical growth in Champia agree in the main with Berthold's, as far as his go. I do not find so great regularity here, however, as Berthold would give one to understand to exist. According to my observations, on looking down upon a tip of the plant, or in examining cross sections of it, a number of rows of cells are to be seen converging towards a common point, the apex (Figs. 4, 5, 6). Three or four of these rows meet at the apex, into the angles formed by them are pushed an equal number of other rows, and the remaining space is filled with a third series. I have found the number of these rows to vary from eleven to fifteen, but always to equal the number of longitudinal filaments in the branch, as Berthold has pointed out (Figs. 6 and 8). The reason for this will be seen when the origin of the latter is understood.

At the head of each of these rows, that is, at the part nearest its apex, there is a cell somewhat larger than those directly beneath it (Figs. 3 and 5). This cell gives rise to others of the row by anticlinal division; that is, by forming partitions at right angles at once to the surface of the frond and to the axis of the row. So each of these cells at the heads of the rows is a true apical cell (Scheitelzelle of the German botanists). Each one is in the shape of a triangular pyramid with rounded sides. The apex of the pyramid is directed inward. while the base lies at the surface of the frond. The length of the pyramid is 10 to 15 \mu, while the width at the base varies from 5 to 10 \mu. The cells formed by the division of the apical cells which are at the middle of the cluster, meet in the middle line below the apical cell And all of these daughter cells, whether they meet in the middle or not, appear somewhat crescent-shaped when close to their apical cell. They do not divide usually until removed several cells from it by division of the apical cell. They then divide, each by a partition parallel to the surface of the frond, at about a fourth or a third of the length of the cell from its inner end (Fig. 3). It is probable that the branches have their origin at this point, as explained later. The outer cell thus formed divides again into two or three cells (Fig. 6), and these may again divide. This division is by means of partitions which are at right angles to the surface of the plant and oblique to the original cell wall. The result of all this is the irregular

mass of cells which forms the cortical layer or wall of the frond. The set of cells derived from each apical cell is easily distinguished within an area of forty micro-millimeters from the apex, because the cells having a common origin are separated from each other within this region by thinner cell walls than those separating cells of different origin, as shown in the figure. Below this area the cell walls become of equal Cell division takes place chiefly within a short distance from the apex; below that, growth takes place principally by enlargement of the cells. Within the area of division the cells are filled with protoplasm and have very evident nuclei. The nuclei in the cortical layer are usually in the lower half of the cell. Below this area around the apex the cells contain large vacuoles and the nuclei become much less prominent, while the protoplasm becomes more coarsely granular. The inner cells above mentioned as the result of the first division below the apex do not divide at right angles to the surface of the plant; at least, if they do, it is a much less frequent process than in outer cells; but many of them, perhaps all, do divide once or twice by partitions parallel to the surface (Fig. 8). As the cortical layer grows, increasing the length and diameter of that part of the frond, these inner cells merely elongate, while they become separated laterally, and so form the longitudinal filaments; as described by Wille for Lomentaria.

By means of the division parallel to the surface just mentioned are produced the "bulb-cells," and the connections behind them with the cortical layers (Fig. 8). The "bulb-cells" attain their adult size very soon after their formation. At intervals of three cells or more, on certain filaments, division is carried further, until the processes pushed out from them in this way meet in the middle of the cavity (Fig. 9). The spaces between these processes are filled by similar ones from the other filaments, and in this way the diaphragm is formed. At first the diaphragm shows very plainly its origin in branches from the filaments. The cells are rounded, contain prominent nuclei, and in short look just like the young filament cells. Then the cells of each of the component branches are separated from each other by thinner walls than those which separate them from the other cells. This formation of the diaphragm occurs about thirty micromillimeters from the surface of the apex. The young disphragm keeps pace with the rapid growth of the adjacent parts of the plant, and thus preserves its continuity, by further cell division and by increase in the size of the cells. These cells finally become polygonal from mutual pressure, the cell walls become equally thick on all sides, and it becomes impossible to distinguish the cells, which had a common origin (Fig. 12). The original filament cell does not increase in diameter with the diaphragm cells, but becomes elongated with the other filament cells (Fig. 2).

It will be observed from the figures that the filaments that come from the apical cells nearest the middle of the cluster (Figs. 5 and 6) show more divisions than the others in the space above the young diaphragm (Fig. 8). The cells derived from them reach the centre of the diaphragm, while the others do not (Fig. 9), and these filaments are the first to give off bulb-cells below the diaphragm (Fig. 10). With the exception of the branches given off to form the diaphragm, the filaments do not branch. Each filament is perfectly simple and straight from its base to the apical cell at the other end.

The question as to the origin of the branches naturally arises now. I have not been able to get the earliest stages, but I am sure they are to be looked for very close to the apex of the plant, for the nearer you get to the apex the smaller branches you find. Occasionally, to be sure, branches a few chambers long may be found below much larger branches; but still I think these are formed earlier than those above them, but are prevented from growth by some accident. It seems probable that the branch will be found to arise by division of one of the outer cells, already described as the result of the cell division close to the apex. At any rate, a branch was seen to spring from a point directly opposite a filament, in all the half-dozen cases that I examined concerning this.

Comparing my description of *Champia parvula* with the description of *Lomentaria kaliformis* by Nägeli and Wille, there will be noticed a striking similarity in general structure and in the details of growth, so far as either Nägeli or Wille describes them, except in regard to the apical cell. Further investigation is necessary to explain this remarkable difference in two species otherwise so much alike.

In order to see if they might throw any light on my subject I have made a hasty examination of some alcoholic material of Champia salicornoides, Harv., from Key West, and of Lomentaria Baileyana. The former has an apical growth identical with that in Champia parvula, and does not differ very greatly in structure from that species. The frond is much larger, but the individual cells are of about the same size. The branches in Champia salicornoides do not come off at the nodes, but may spring from any part of the internodes. At the base of each branch is a layer of cells smaller than those in the wall of the main stem, but it is apparently a continuation of that structure. Then

inside of this is a circular patch of rounded cells twice as large as the ordinary cells of the wall. So that the basal chamber of the side branch is separated from the chamber of the main branch by two layers of cells. There are a good many more filaments in this species than there are in *Champia parvula*, and each filament has about seven cells to a chamber. On each of the filament cells except those piercing the diaphragms there is a bulb-cell, or there may be a pair of them together. The cells that connect the filaments with the cortical layer are sometimes enlarged, and bear bulb-cells similar to those on the filaments. The branches spring from a cortical layer directly opposite a filament, as in *Champia parvula*, and in the one specimen that I examined on this point I found a bulb-cell at the centre of the base of the branch.

Lomentaria Baileyana is very different from Champia. There are no diaphragms in the frond except across the base of the branches. Inside the cortical layer, which resembles the one in Champia, is a network with rather small meshes, composed of oblong cells whose long axes run more or less obliquely in the direction of their part of the plant. Inside of this network is another, with large meshes, and formed by slender crooked and branched filaments, on which are found occasionally bulb-cells like those in Champia. The filaments seem to come together at the tip in a sort of tuft, in which I can see no regular order.

I have also examined some dried material of Lomentaria Coulteri. The main stems of this plant are without constrictions and solid, while the small side branches are chambered, and superficially resemble Champia. The whole plant is covered with a cortical layer of small columnar cells, well filled with protoplasm, and containing the coloring matter. The bulk of the main stem is of ordinary parenchyma, the cells containing but little protoplasm. The chambered branches have a single layer of this tissue lining the cortex, and it also forms the single-layered diaphragms. The filaments in the chambered portion somewhat resemble those in Lomentaria Baileyana, but resemble more closely those in Champia parvula. They plainly converge to a point at the apex of the branch; but just what the structure is there, the material was insufficient to show.

We have to leave our subject for the present in an unsettled, and therefore rather unsatisfactory condition. In order to get a complete understanding of these hollow-fronded sea-weeds, the development of one or more of them must be traced from the spore to the adult stage. The present paper can, however, lay claim to having added its little to our knowledge of these plants, in making clear, — 1. That in the case of Champia parvula the apical growth is not from a single apical cell, but, as Berthold has pointed out, from a cluster of them; 2. That each of these apical cells is morphologically at the tip of one of the longitudinal filaments; 3. That in the three or four cells which seem to be morphologically the tip of the filament each cell divides, part going to form parts of the adult filament, the rest to join in the formation of the cortex; 4. That the diaphragms and bulb-cells are alike in origin, in being formed by outgrowths from the filaments; and, 5. It would appear from the limited number of observations made on this point that the branches always have their origin opposite a filament.

#### NOTE.

In October, 1886, Mr. Bigelow, then a candidate for the degree of Bachelor of Science, undertook, at my suggestion, the investigation the results of which are given in the preceding pages. At the time, I was not aware that any other botanist was working on the same subject, and it was not until April, 1887, that I learned from the "Botanisches Centralblatt" that Professor F. Debray had just published a paper entitled "Recherches sur la Structure et le Développement du Thalle des Chyclocladia, Champia et Lomentaria," covering the same ground as that on which Mr. Bigelow was at work. I was unable to obtain a copy of the original paper of Professor Debray, published in the "Bulletin Scientifique du Département du Nord." IX. 258-266, until late in May, and as at that time Mr. Bigelow had practically finished his work, it seemed to me best that he should publish his results, although they were in accord with those of Professor Debray. It should be said, in explanation of the omission by Mr. Bigelow of any reference to Professor Debray's paper, that he did not see a copy of it until after his own paper was quite finished and in my hands for publication. Had I known at an earlier day that Professor Debray was at work on this subject, I should, of course, have suggested a different topic to Mr. Bigelow. As it is, his work is a confirmation of previous results reached quite independently, because, as I have said, he was in complete ignorance of what had been written by Professor Debray until after his article was finished.

W. G. FARLOW.

### ACADEMY

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## EXPLANATION OF THE PLATE.

All the figures are of *Champia parvula*. Fig. 2 is from a free-hand section mounted in glycerine and acetic acid. It is drawn chiefly with the cameralucida, but in places is slightly diagrammatic. The other figures are strictly camera-lucida drawings. Those beyond Fig. 2 are made from stained microtome sections mounted in benzol balsam.

- Fig. 1. A small branch, with a portion of the larger one from which it sprang.  $\times$  4°.
- Fig. 2. Interior view of the upper portion of a branch. a, apex; b, bulb-cell; c, cortex; d, diaphragm; f. filament; e, connection between the filament and the cortex.  $\times 14^{\circ}$ .
- Fig. 3. Longitudinal section of a tip passing through the apex. a, apical cell; the other letters as above.  $\times$  <sup>2</sup>§<sup>2</sup>.
- Figs. 4-10. A series of transverse sections from a single tip. They are about  $5\mu$  thick. Figs. 4-7 are a continuous series, Fig. 4 being the extreme tip. Figs. 8 and 9 are the sixth and seventh sections of the series, and Fig. 10 is the tenth. Figs. 4, 5, and 6 show the converging rows of cells, each headed by an apical cell. In Fig. 7 we get the beginning of the cavity. Fig. 8 shows the condition just above the young diaphragm, which appears in Fig. 9. Fig. 10 is the first section that cleared the diaphragm below. By comparing with Fig. 3, it will be seen that these sections are oblique to the axis of all the cells in them, except those very near to the middle of the section. 1, 2, 3, etc., indicate corresponding areas in the different sections.  $\times$  249.
  - Fig. 12. Transverse section of another branch through the third diaphragm.
- Fig. 11. Second section above Fig. 12. In these two sections we have very nearly the adult condition.  $\times \frac{140}{1}$ .

## VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE. - J. P. COOKE, Director.

## SILICOTETRAFLUORIDES OF CERTAIN BASES.

BY ARTHUR M. COMEY AND F. W. SMITH.

#### Presented November 8, 1887.

SUPPLEMENTARY to the investigations \* made by C. Loring Jackson and one of us on the action of fluoride of silicon on organic bases, we have further tried the action of fluoride of silicon on nitrosodimethylaniline, pyridine, cinchonine, and quinine.

Trinitrosodimethylaniline disilicotetrafluoride, (C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>)<sub>3</sub>(SiF<sub>4</sub>)<sub>2</sub>.

— This compound was formed by passing fluoride of silicon through a solution of the base in benzol. A lemon-yellow precipitate was formed, which was washed thoroughly with benzol and dried at 100°. The following results were obtained from the analysis of this product:

0.1822 grm. of the substance gave 0.0345 grm. of silicic dioxide and 0.0936 grm. of sodic fluoride.

	Calculated for	
	(C <sub>2</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>3</sub> (SiF <sub>4</sub> ) <sub>3</sub> .	Found.
Silicon	<b>8.54</b>	8.83
Fluorine	23.09	23.25

Trinitrosodimethylaniline disilicotetrafluoride is a bright yellow amorphous powder, which is decomposed by water, with separation of silicic dioxide, and decomposes completely with slight explosion when heated above 150°.

Dipyridine silicotetrafluoride, (C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>SiF<sub>4</sub>.— This substance was prepared by passing fluoride of silicon through a solution of pyridine in benzol, whereupon it separates out in the form of a heavy voluminous precipitate, which when washed with benzol and dried, and immediately analyzed, gave the following results:

<sup>\*</sup> Ante, p. 20.

0.3132 grm. of the substance gave 0.0925 grm. of silicic dioxide and 0.2039 grm. of sodic fluoride.

	Calculated for	
	(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> SiF <sub>4</sub> .	Found.
Silicon	10.77	10.81
Fluorine	29.00	29.45

Dipyridine silicotetrafluoride is a pure white amorphous powder, which decomposes upon standing, giving off pyridine and forming tripyridine disilicotetrafluoride.

Tripyridine disilicotetrafluoride,  $(C_5H_5N)_3(SiF_4)_2$ . — This compound is formed by subliming the previous substance. Pyridine is given off and tripyridine disilicotetrafluoride sublimes, forming a crust possessing a distinct crystalline structure. It is extremely deliquescent and was not obtained in a pure state for analysis. The following results of the analysis of the slightly deliquesced substance leave no doubt as to its true constitution.

0.1743 grm. of the substance gave 0.0443 grm. of silicic dioxide and 0.1248 grm. of sodic fluoride.

	Calculated for	
	(C <sub>8</sub> H <sub>8</sub> N) <sub>3</sub> (SiF <sub>4</sub> ) <sub>2</sub> .	Found.
Silicon	12.68	11.86
Fluorine	34.14	32.16

When fluoride of silicon was passed into the ethereal solutions of cinchonine or quinine, a gummy substance separated, which probably possessed a constitution similar to that of the above substances.

The constitution of these substances has been discussed at length in a previous paper \* by C. Loring Jackson and one of us. It remains only to add, that the compounds of which disniline silicotetrafluoride is the type seem to be formed first. These are very unstable, giving up one molecule of the base with the greatest ease to form compounds corresponding to trianiline disilicotetrafluoride. This extra molecule of the base in most cases is separated by merely washing with a solvent as benzol, as in the case of aniline, toluidine, diphenylamine, chinoline, etc. In others, as dimethylamine and pyridine, the extra molecule is only given off upon standing, or by the action of heat.

Boron trifluoride gave products with organic bases which apparently possess an analogous constitution, but the substances formed were not further investigated.

<sup>\*</sup> Ante, p. 82.

According to Schiff,\* stannic tetrachloride forms an addition product with aniline, of the composition (C<sub>6</sub>H<sub>7</sub>N)<sub>4</sub>,SnCl<sub>4</sub>. With diphenylamine, however, we obtained by the action of stannic tetrachloride a product, melting at 180–181°, containing no tin; chlorine was present in large quantity. The investigation of the action of stannic tetrachloride on organic bases will be continued by one of us.

The above work was done in the Summer School of Chemistry at Harvard College.

<sup>\*</sup> Jahresbericht, 1863, p. 412.

## VIII.

## AN EMPIRICAL RULE FOR CONSTRUCTING TELE-PHONE CIRCUITS.

## By WILLIAM W. JACQUES.

#### Presented June 15, 1887.

THE following paper describes some investigations I have made as to the proper dimensions to be given to pole lines and cable conductors, in order that they shall be best fitted to transmit speech telephonically.

The experiments were made by selecting cables varying in size of conductor, thickness of insulating coating, and material used for insulating, and measuring in each case the greatest length in miles through which good business conversation could be carried on.

Similar experiments were then made with pole lines, in which the size of the wire was varied, the distance it was suspended above the earth was varied, and both iron and copper wires were used.

Further experiments were then made in which mixed cable and pole lines were used, varying the proportionate length of cable to pole line in each case, and also the position of the cables in the line.

These experiments were made upon a large number of underground cables, varying in length from one mile to one hundred miles, in resistance per mile from 2.8 ohms to 48.0 ohms and in electro-static capacity per mile from 0.11 microfarad to 0.35 microfarad, in use in France and Germany, (an abstract of which was published in the Proceedings of the Society of Arts of November 13, 1884,) and were continued upon a large number of cables and pole lines in our own country.

The method of experiment was to connect up varying lengths of cable or pole line until the greatest length at which it was possible to transmit good business conversation was reached, and then to measure the electrical resistance and capacity of the circuit.

Some of the experiments are given in Tables I. to IV., to illustrate the method of experiment, and prove the results stated later.

TABLE I. - EXPERIMENTS ON CABLES.

	Longth	Registance	Capacity new Mile in	Total	Total	Product of total Registrance	Quality o	Quality of Talking.
	io Mile.	Ohms.	Microfarada	Recistance.	Capacity.	by total Capacity.	Blake.	Hunnings.
Paris Telephone Wires.	e.	848	0.16	240	0.80	192	Good talking.	Good talking.
2	91	48	0.16	480	1.60	168		
= = =	16	848	0.16	720	2.40	1,728	,	"
;	ଛ	84	0.16	98	8.20	3,072	Experts could talk.	:
3	8	84	0.16	1,440	4.80	6,982	Could not talk.	Experts could talk.
3 3	<del></del>	<b>8</b>	0.18	1,680	2.60	9,408	*	" "

TABLE II .- EXPERIMENTS ON CABLES.

	Distance	Resistance	Capacity	Total	Total	Product of total	Quality of Talking.	Talking.	
	in Miles.	Obms.		Resistance.	Capacity.	by total Capacity.	Blake.	Hunnings.	
Paris and Orleans (Gov. Telegraph).	<b>38</b>	13.8	0.07	1,181	98.9	6,729	Could not talk.	Experts could talk.	
3	88	8.6	0.11	781	9.82	6,835	=======================================	" "	_
,	88	4.3	0.20	365	17.0	6,189	2 2	"	
,,	88	2.87	0.31	244	26.35	6,429	:		_
Paris and Soissons.	99	9.6	90.0	624	3.90	2,434	= =	Good talking.	
* * *	8	16.0	90.0	1,040	8.25	8,880	Experts could talk.	, ,	
German Cables.	81	121	0.85	375	10.85	4,060	Could not talk.	,	

TABLE III. - EXPERIMENTS ON POLE LINES.

	Distance	Recistance		Total	1	Product of	Quality of Talking.	Talking.
	talked in Miles.	per Mile in Ohms.	per Mile in Microfarade.	Registance.	Capacity.	ance by total Capacity.	Blake	Hunnings.
Boston and New York, Copper.	800	9	210.	1,600	8.6	5,400	Could not talk.	Experts could talk.
Boston and Providence, Copper.	62	ō	.012	260	.624	162	Good talking.	Good talking.
Bostonand New Haven, { Copper.	191	9	.012	955	8.8	2,674	Experts could talk.	3
Boston and Providence, \ Iron.	23	19.6	.016	1,020	.78	962	Good talking.	3
Boston and Newbury-	æ	83	.017	1,000	6.	006	;	;
Boston and Rye Beach, Iron.	8	8	.018	1,600	1.5	2,400	Only experts could	;
Boston and New Haven, { Iron.	191	20	.017	8,820	3.25	12,600	could not talk.	Could not talk.

TABLE IV. -- MIXED CABLE AND POLE LINES.

Palking		Hunnings.	Good talking.	Good talking.	Good talking	Suratus non				
Quality of Talking.		Blake.	Experts could talk.	"	Good talking.	.0	Experts could talk	Could not talk	Good talking	Could not talk.
Product	Resistance	Pole by total Wire. Capacity.	2,204	2,863	1.711	535				
Total	Jo Of	Pole Wire.	.42	83	88.	120.	.021	.021	182	.182
Total	Capacity	Cable.	4.20	1.15				•		3.30
		Pole Wire.	822	1465	1465	29.4	29.4	29.4	333	255
Total	8008	of Cable.	156	83	63	280	88	870	88	280
Capacity ner Mile	5	Pole Wlre.	.021	.018	.013	.014	10.	.014	.014	.014
Capacity	per Mile	Cable.	38.	.46	53	S.	ģ	S,	æ	.83
Regist- Regist-	Mile of	Pole Wire.	19.1	:	:	19.6	19.6	19.6	19.6	19.6
	ě	Mile of Cable.	12.9	52	22	89	88	88	8	58
3	9	Poles.	ន	8	೫	14	1	=	13,	18
X.	٥	Cable.	12	<del>1</del> 2 ~~	<b>2</b>	<u>ت</u>	2	16	9	10
			Block Island Line.	Pittsburg (Standard Star).	Pittsburg(Patterson).	Attleborough.	3	ť	*	ų

Tables I. and II. give the results of some experiments made on cables; Table III., on pole lines; and Table IV., on mixed cables and pole lines. The numbers showing the total resistance and total capacity refer to the line between the terminal instruments, and do not include the terminal instruments.

I find from these experiments, that the readiness with which telephonic conversation may be carried on over any circuit, whether made up of cables or pole lines, or both, depends,—

- 1. On the total electrical resistance of the circuit joining together the two stations.
  - 2. On the total electrostatic capacity of this circuit.

So long as the insulation is sufficiently good to prevent any considerable loss of current, its actual value, whether high or low, does not affect the readiness with which conversation may be carried on. High insulation is desirable, however, when two or more wires run near together, in order to prevent extraneous currents from leaking in and causing disturbing nois's.

The distance over which telephonic conversation may be carried on, being thus dependent on the resistance of the circuit and on the capacity of the circuit, (being inversely proportional to each of these,) is dependent upon their product, and this product has a definite numerical value for each kind of transmitter used, being 4,500 for transmitters of the Hunnings type, and 2,000 for transmitters of the Blake type; that is, the product of the total resistance of the current between two telephones, by its total capacity, must not exceed 4,500 if transmitters of the Hunnings type be used, and must not exceed 2,000 if transmitters of the Blake type be used. These results suppose the ordinary Bell hand telephone to be used as a receiver, but are not essentially varied by the use of other good forms of magneto receiver. These limits are given for good business conversation. It is of course possible for experts to get messages through circuits the product of whose resistance and capacity is somewhat greater than this.

The resistance and capacity measured should be, as stated, that of the line between the two telephones. It includes, of course, the resistance and capacity of any way station switchboards or call bells. It does not include the resistances of the terminal telephone instruments used.

These results may be briefly formulated in the following rule: —

"No matter what may be the distance between two points, good business conversation may be carried on between them, provided they be connected by a pole line or cable, or both, the product of whose total resistance by its total capacity is less than 2,000 if transmitters of the Blake type be used, and less than 4,500 if transmitters of the Hunnings type be used."

This rule is purely the result of experiment. It applies to a single conductor joining together the two telephones, and is equally applicable whether the return circuit is completed through the earth or by means of a second wire similar and parallel to the first. It supposes the line to be ordinarily free from extraneous noises, and, as in positions especially liable to extraneous noises metallic circuits would naturally be used, it is in all cases a perfectly safe working rule.

Having thus determined the general rule above annunciated, we must be able to apply it to specific cases; as, for example, to write a specification for a line which is to connect two cities one hundred miles apart, and which is to pass from the centre of each city underground, two miles, to the suburbs.

In order to do this, we need to know the resistance per mile of various sizes of wire, whether of iron or copper, and excellent tables are published in various text-books giving these figures. I have, for convenience, printed the resistances of various sizes of iron and copper wire in the annexed Tables V. and VI.

TABLE V. - IRON WIRE.

. No. В. W. G.	Diameter in Inches.	Ohms per Mile.	Feet per Mile.
0000 000 00 0 1 2 8 4 5	.454 .425 .880 .840 .300 .284 .259 .238	1.70 1.95 2.43 8.88 8.91 4.36 5.24 5.51 7.26	8108 2708 2172 1878 1350 1211 1008 958 727
6 7 8 9 10 12 14 16 18	.203 .180 .165 .148 .134 .109 .083 .065	8.54 10.86 12.92 16.10 19.60 29.60 51.00 83.20 147.00	618 578 409 828 269 179 104 63 85.9

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No. B. W. G.	Diameter in Inches.	Ohms per Mile.	Foot per Mile.
5	.220	1.128	4681
6	.203	1.325	8986
7	.180	1.684	8185
8	.165	2.005	2634
9	.148	2.492	2120
10	.184	3.040	1737
11	.120	3.791	1898
12	.109	4.594	1149
13	.095	6.048	878
14	.083	7.936	665
15	.072	10.529	502
16	.065	12.918	408.7
17	.058	16.99	310.8
18	.049	22.73	232.3
19	.042	30.94	170.6
20	.035	44.55	118.5
22	.028	69.62	75.8
24	.022	112.77	46.8

TABLE VI -- COPPER WIRE.

But we need also to know the capacity per mile of various sizes of pole wire when suspended at various heights above the earth, (for the capacity of a pole wire depends both upon its size and the distance it is suspended above the earth,) and we need further to know the various capacities of various sizes of cable conductors when insulated to various thicknesses, and when insulated with various substances; for the capacity of a cable conductor depends upon its size, upon the distance it is removed from neighboring conductors by the thickness of the insulating coating, and upon the specific inductive capacity of the particular insulating coating used.

Now the available data regarding capacities of pole lines and of cables (excepting ocean telegraph cables which have only one conductor, and in which the conductors are quite different from that of the multiple conductor cables used in telephony) are very meagre, and I have therefore been obliged to undertake an experimental investigation into the capacities of wires of different sizes, suspended on poles of varying heights, and a further investigation into the capacities of various sizes of cable conductors when separated from the neighboring conductors by varying thicknesses of insulating material, and when insulated with various materials differing in specific inductive capacity.

The results are given in Tables VII., VIII., and IX.

TABLE VII. -- CAPACITIES OF POLE WIRES.

Ŋ,	Dlameter					Helg	Height of Pole in Feet.	Foot.				
B. W. G.	Inches.	30.	88.	.74	.98	88	80.	33.	34.	86.	88	<b>4</b> 0.
000	.454	.0149	.0147	.0145	.0144	.0148	.0142	.0141	.0189	.0138	.0137	.0186
8	.425	.0148	.0146	.0144	.0148	.0142	.0141	.0140	.0188	.0137	.0136	.0136
8	988.	.0147	.0144	.0143	.0141	.0140	.0138	.0137	.0136	.0135	.0186	.0184
•	.340	.0144	.0141	.0141	.0189	.0138	.0136	.0185	.0186	.0134	.0138	.0132
-	.300 .300	.0142	.0140	.0188	.0137	.0136	.0135	.0184	.0183	.0132	.0131	.0130
64	284	.0140	.0139	.0137	.0136	.0135	.0184	.0188	.0182	.0131	.0130	.0129
တ	.259	.0139	.0137	.0135	.0185	.0134	.0182	.0130	.0130	.0129	.0129	.0128
4	883	.0187	.0136	.0184	.0134	.0182	.0181	.0129	.0129	.0128	.0127	.0127
9	220	.0138	.0135	.0138	.0182	.0131	.0130	.0127	.0128	.0127	.0126	.0128
9	.203	.0135	.0134	.0132	.0131	.0130	.0128	.0128	.0127	.0128	.0126	.0125
2	.180	.0133	.0132	.0180	.0129	.0128	.0127	.0125	.0125	.0125	.0124	.0128
80	.165	.0131	.0131	.0129	.0127	.0127	.0126	.0123	.0124	.0123	.0122	.0122
6	.148	.0130	.0128	.0127	.0126	.0125	.0126	.0122	.0122	.0122	.0121	.0120
2	.134	.0128	.0127	.0128	.0125	.0124	.0123	.0120	.0121	.0120	.0119	.0119
13	.109	.0128	.0124	.0128	.0122	.0121	.0120	.0116	.0119	.0118	.0118	.0117
14	.088	.0122	.0120	.0120	.0119	.0118	.0117	.0118	.0116	.0115	.0114	.0118
16	.065	.0119	.0118	.0117	.0116	.0116	.0114	.0113	.0112	.0112	.0112	.0111
18	.0 <del>4</del> 9	.0116	.0114	.0118	.0112	.0111	.0111	.0110	.0110	.0109	.0108	.0108

TABLE VIII. — CAPACITIES. GUTTA-PERCHA CABLES.

(Spf. Ind. Capacity = 42.)  $C = \frac{0.1628}{\log \frac{2d+4}{d}}$ .

Number of Lancetten Coordinates of Lanusting Continue (= $7$ ). Coordinates (= $7$ ). And Number of Lanusting Continue (= $7$ ). And Number of Lanusting Conti											3					
W.G.         1.01 (1) (1) (1) (1) (1) (1) (1) (1) (1) (1	Number of Conductor	Conductor					Th	ickness of	Insulating	Coating in	Inches (=	IJ.				
300         .456         .457         .429         .404         .382         .364         .384		in Inches $(=d)$ .	.01.	.03.	.03.	.04.	.05.	.06.	.07.	.08.	.09.	.10.	.13.	.15.	.80.	.85.
284         493         464         424         389         378         369         343         389         381         389         381         389         381         389         381         389         381         389         381         389 <td>-</td> <td>906.</td> <td>.496</td> <td>.457</td> <td>.429</td> <td>404</td> <td>388</td> <td>.364</td> <td>.349</td> <td>.334</td> <td>.824</td> <td>.312</td> <td>.293</td> <td>.270</td> <td>.248</td> <td>.224</td>	-	906.	.496	.457	.429	404	388	.364	.349	.334	.824	.312	.293	.270	.248	.224
256         480         448         416         389         389         3849         383         324         307         299         278         256         230           238         484         441         409         382         569         341         324         311         208         289	83	284	.493	.454	.424	888	.378	.359	.343	.829	.317	908.	287	.265	.238	219
238         484         441         409         382         384         311         208         288         289         289         311         208         289         289         281         311         324         311         329         312         312         312         313         389         294         289         270         270         270         282         241         211           200         470         480         380         381         381         388         294         288         271         265         234         210           180         470         480         382         380         311         296         288         270         260         271         265         281         281         281         282         281         282	80	359	.490	.448	.416	.389	808	.849	.833	.824	.307	299	.278	.256	.230	212.
230         481         487         402         373         382         317         308         290         270         205         241         217         262         241         217         262         244         210         203         311         296         283         270         286         271         265         234         210         271         265         234         210         271         265         284         210         271         265         284         271         265         284         271         265         284         271         265         284         271         265         284         271         265         284         272         262 <td>₹</td> <td>823</td> <td>.484</td> <td>.441</td> <td>408</td> <td>.382</td> <td>.369</td> <td>.341</td> <td>.324</td> <td>.811</td> <td>208</td> <td>.288</td> <td>569</td> <td>.249</td> <td>.225</td> <td>506</td>	₹	823	.484	.441	408	.382	.369	.341	.324	.811	208	.288	569	.249	.225	506
208         476         480         385         342         318         308         294         288         271         256         234         210           1.80         470         421         382         353         311         226         283         270         260         244         224         271           1.66         466         413         373         344         317         382         287         273         262         252         252         252         236         217         136           1.148         454         486         383         380         281         287         262         252         252         236         237         136         136           1.134         454         384         387         286         286         266         246         242         226         227         136	6	220	.481	.437	.402	.373	.852	.382	.817	808.	.290	.279	262	.241	217	.200
186         470         421         382         353         380         311         296         283         270         286         284         224         284         284         281         282         287         283         287         287         282         283         287         282         287         283         287         284         383         381         381         286 <td>6</td> <td>203</td> <td>.478</td> <td>.480</td> <td>.889</td> <td>.865</td> <td>.842</td> <td>.318</td> <td>808</td> <td>.294</td> <td>.288</td> <td>.271</td> <td>255</td> <td>.234</td> <td>.210</td> <td>.194</td>	6	203	.478	.480	.889	.865	.842	.318	808	.294	.288	.271	255	.234	.210	.194
166         466         413         373         344         317         382         287         273         262         252         252         252         252         253         310         291         291         276         268         262         252         242         252         272         273         317         196           134         454         384         385         380         286         286         268         268         268         268         252         212         274         278         278         378         187         187         180         188         180         188         188         189         278         226         226         216         226         226         212         226         227         188         188         188         188         188         188         188         188         188         188         188         188         188         188         188         188         189         188         189         189         189         189         189         189         189         189         189         189         189         189         189         189         189         189	2	.180	.470	.421	.882	.353	.880	.311	967	.283	.270	.260	244	.224	201	.185
148         457         402         363         310         291         276         268         262         242         252         242         254         255         254         255         254         255         254         255         256 <td><b>∞</b></td> <td>.165</td> <td>.465</td> <td>.413</td> <td>.873</td> <td>.344</td> <td>.817</td> <td>.382</td> <td>287</td> <td>273</td> <td>.262</td> <td>.252</td> <td>.236</td> <td>217</td> <td>195</td> <td>.180</td>	<b>∞</b>	.165	.465	.413	.873	.344	.817	.382	287	273	.262	.252	.236	217	195	.180
.134         .454         .894         .863         .807         .299         .286         .266         .264         .248         .274         .219         .286         .265         .246         .236         .226         .216         .226         .216         .202         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .186         .187         .186         .187         .181         .184         .184         .184         .184         .184         .184         .184 <th< th=""><td>0</td><td>.148</td><td>.457</td><td>.402</td><td>.863</td><td>.333</td><td>.310</td><td>162</td><td>276</td><td>.263</td><td>.252</td><td>242</td><td>.226</td><td>.208</td><td>.187</td><td>.173</td></th<>	0	.148	.457	.402	.863	.333	.310	162	276	.263	.252	242	.226	.208	.187	.173
.109         .438         .873         .382         .801         .279         .246         .225         .225         .226         .226         .227         .246         .253         .263         .263         .222         .212         .203         .196         .183         .169         .153           .065         .390         .320         .279         .261         .281         .212         .202         .194         .184         .186         .179         .168         .163         .163         .163         .163         .163         .163         .163         .162         .162         .162         .162         .162         .179         .184         .172         .114         .184         .1	91	.134	454	.894	.853	.807	538	286	.286	254	.248	<b>28</b> 2	.218	.201	.180	.167
.083         .418         .346         .303         .268         .226         .226         .212         .203         .106         .163         .169         .153           .065         .390         .320         .279         .261         .281         .216         .208         .194         .184         .176         .166         .162         .162         .141           .049         .361         .201         .261         .226         .208         .194         .184         .176         .166         .162         .162         .142         .129           .086         .388         .261         .221         .199         .188         .172         .166         .144         .186         .127         .117           .028         .304         .281         .181         .181         .169         .161         .161         .144         .186         .177         .117         .119         .118         .119         .119         .119         .109         .109         .169         .161         .161         .184         .181         .181         .110         .109         .161         .161         .184         .181         .181         .110         .109         .161	12	.109	.438	.873	.832	.301	972.	265	246	235	225	.216	202	.186	.168	.166
.065         .380         .320         .279         .251         .281         .216         .208         .194         .186         .176         .186         .176         .186         .176         .162         .162         .162         .142         .129           .049         .361         .201         .216         .194         .184         .176         .162         .162         .162         .142         .129         .129           .086         .328         .261         .221         .189         .183         .172         .162         .164         .144         .186         .127         .117         .117         .144         .139         .184         .181         .109         .109         .169         .161         .164         .184         .186         .117         .119         .184         .181         .110         .109         .109         .161         .164         .184<	14	.083	.418	.346	.303	.263	.253	823	222	212	.203	.195	.183	.169	.153	.142
.049     .361     .221     .226     .208     .194     .184     .175     .165     .165     .162     .162     .162     .162     .163     .175     .164     .184     .184     .184     .184     .187     .127     .117       .028     .304     .287     .204     .181     .169     .161     .144     .139     .184     .187     .119     .109	18	.065	.390	320	.279	.251	.231	.216	203	194	.186	.179	.168	.166	.141	.131
.085     .828     .261     .221     .199     .183     .172     .162     .166     .149     .144     .186     .127     .117     .117       .028     .804     .287     .204     .181     .169     .161     .161     .144     .139     .184     .127     .119     .109     .109	18	.049	.361	291	.251	.226	208	194	.184	.175	.165	.162	.152	.142	.129	.120
. 804 . 287 . 204 . 181 . 181 . 189 . 151 . 151 . 151 . 189 . 181 . 184 . 184 . 189 . 184 . 189	8	.085	.828	.261	122.	.199	.183	.172	.162	.156	.149	.144	.186	.127	.117	.109
	22	880.	.80 <del>4</del>	.287	.204	181.	.169	.159	.161	.144	.139	.184	.127	.119	.109	.103

TABLE IX. -- CAPACITIES. INDIA RUBBER CABLES.

(Spf. Ind. Capacity == 8.7.)

Number	Diameter					T T	kness of I	Thickness of Insulating Coating in Inches (=	deting in ]	Inches (=	Ė				
B. W. G.	in Inches $(=d)$ .	.01.	.0%.	.08.	.04.	.05.	.06.	.07.	.08.	.60	.10.	.18.	.15.	.30.	.35.
-	.300	.436	.402	.378	858	386	.820	.807	294	286	275	.258	.288	.214	.197
87	284	.484	<del>4</del> 00	.378	.861	888.	.816	305	290	279	508	.253	288	.209	.193
8	259	.481	894	898.	.842	.824	.807	293	286	.270	283	.246	226	202	.187
4	.238	426	.388	.860	.836	.816	98.	285	274	262	.253	287	219	.198	181
4	220	.428	386	.354	.828	.810	282	.279	.267	.255	.246	183	212	191	.176
•	203	419	.378	.842	.821	.801	275	271	.259	.249	883	.224	908	.185	.171
2	.180	414	.870	888.	.311	280	274	986	249	238	528	216	.197	.177	.163
∞	.165	409	386	.326	.903	279	.266	.258	.240	.231	222	508	191	.172	.158
6	.148	.402	.358	.317	293	278	256	243	123	222	.218	.199	.183	.165	.152
2	.134	.400	.847	808.	.270	268	252	.234	.224	.214	.196	.192	771.	.158	.147
12	.109	386	.328	280	265	246	883	217	207	.198	.190	.178	.164	.148	.186
14	.083	383	305.	286	.231	.228	208	.196	.187	.179	.172	191.	.149	.135	.128
16	990	.348	282	.246	123	203	.190	.179	171.	.164	.158	.148	.136	.124	.116
18	.049	.818	.256	221	.199	.183	171.	.162	.154	.145	.148	.184	.125	.114	.106
8	.085	289	230	1961	.175	191.	.151	.143	.187	.139	.127	.120	.112	.108	980
ន	820:	288	200	.180	.169	.149	.140	.183	.127	.12g	.118	.112	.106	980.	.091

TABLE X. -- CAPACITIES. PARAFFINE CABLES.

(Spf. Ind. Capacity == 2.52.)

Number of						T.	ckness of I	nsulating (	Thekness of Insulating Coating in Inches (=	Inches (=	ę				
B. W. G.	in Inches $(=d)$ .	.01.	.0%	.08	9.	.05.	.06.	.07.	.08	.09.	.10.	.18.	.15.	.80	.85.
-	.300	887	.274	.257	242	229	.218	.209	200	.194	.187	176	.162	.146	.184
81	284	296	272	.254	.289	7227	215	206	197	.190	184	.172	.159	.143	.131
<b>∞</b>	.259	<b>2</b> 83	.269	.250	238	122:	608.	200	.194	.184	179	.167	.164	.188	.127
4	.238	280	265	246	229	.216	.205	.194	.187	921.	.178	191.	.149	.136	.124
æ	.220	388	262	.241	.224	211	.199	.190	.182	.174	.167	.167	.146	.180	.120
8	208	88.	.258	.238	.219	.206	.188	.186	921.	.170	.163	.163	.140	.128	.116
7	.180	282	.253	229	212	.198	.187	.175	.170	.162	.156	.146	.134	121.	.111
80	.165	278	.248	224	508	190	.180	.172	.164	.167	.161	.142	.130	711.	.108
۵	.148	.274	.241	.218	200	.186	.176	.166	.158	.161	.146	186	.126	.110	.104
92	.134	272	286	212	184	.179	.172	.160	.152	.146	.140	.131	.121	.108	.100
12	.109	288	224	.199	181	.167	.169	.148	.141	.136	.130	121.	.112	101	960.
14	880:	248	808	.182	.158	.162	.142	.133	.127	.122	.117	.110	.102	.092	.085
16	386	284	.192	.167	.151	.139	.180	.122	911.	.112	.108	101.	860.	.086	920.
18	040	217	.176	.161	.186	.126	.116	.110	301.	660	260	.091	980.	.079	.072
8	.036	.197	.167	.183	911.	.110	.103	760.	.094	680	980.	.082	920.	070.	.065
83	88	.182	.142	.122	.109	101	980	100	980.	.083 83	080	720.	120.	.067	.062

Table VII. gives the capacities of wires from No. 0000 B. W. G. to No. 18, when suspended above the ground at heights varying from 20 feet to 50 feet.

Of course I have not measured the capacity of each size of wire at each height, but I have chosen a large variety of sizes and heights, and, having measured these, have calculated the remainder from these by means of the formula

$$C = \frac{k \, l}{\log \frac{4 \, h}{d}},$$

in which

C =capacity of the lines in microfarads.

l = length of line in miles.

h = height above the earth in inches.

d = diameter of lines in inches.

k = the number .0496, i. e. the capacity of such a wire that

$$\frac{I}{\frac{\log 4h}{d}} = \text{unity}; \text{ this number } (k) \text{ being calculated from such}$$

wires as were actually measured.

The capacity of any wire not given in the table may be calculated from this formula.

The capacities thus obtained apply to a single wire on a line of poles. If there are other wires on the same poles, a correction must be added depending upon the number of such wires, and their distance apart.

For the ordinary case we meet with in telephony — i. e. a considerable number and placed about 18 inches apart — a sufficiently accurate correction may be obtained by adding 50%.

Table VIII. gives the capacities of different sizes of wire from No. 4 to No. 22 B. W. G., when insulated with successive thicknesses of gutta-percha from .01 inch to .25 inch, and combined into cables of fifty conductors and enclosed in a metallic sheath.

Table IX. is a similar table, in which India-rubber is used for insulating; and Table X. one in which the conductors of the cable are insulated with cotton so impregnated with paraffine as to be homogeneous. This table is applicable to the so-called Patterson cable if the values be increased by 60%.

These tables were prepared by measuring a wide variety of cable conductors differing in size of conductor, thickness of insulating material, and kind of insulating material, and calculating the remaining values from the measured values by the formula

$$C = \frac{NLI}{\frac{\log 2s}{d}} = \frac{NLI}{\frac{\log 2d + 4T}{d}},$$

in which

C = capacity of the conductor in microfarads.

s = average distance between centres of adjacent conductors.

d = diameter of conductor.

T = thickness of insulating coating of any one conductor.

L =length of conductor in miles.

I = specific inductive capacity of insulating material used.

N= the number 0.0387, i. e. the capacity of one mile of such a wire

that 
$$\frac{I}{\frac{\log 2 s}{d}}$$
 = unity.

The number N is calculated from values reached by experiments on a large number of conductors.

The capacity of any cable conductor not given in these tables, and insulated with any material whose specific inductive capacity is known, may be calculated from this general rule.

Having thus determined a general rule for the construction of any telephone circuit, and having provided in the foregoing tables data by which the rule may be applied, I will give an illustration, by applying it to the particular case above cited, namely a telephone line between two cities one hundred miles apart, entering each city by underground cables two miles in length.

Let us further suppose that the subscriber is in each case connected to the central office by a mile of underground cable, and that at each central office, there is a multiple switchboard, any connection through which has a resistance of 25 ohms, and a static capacity of .10 microfarad.

It is desired to use Blake transmitters.

## RESISTANCE.

Line of No. 13	cor	ppe	r o	n 3	0 ft	. p	oles	, 6.	048	×	96		•		571
Cable of No. 1	8 in	su	late	d v	vith	k	erite	to	No.	10,	22	.7 >	ς 6		136
Switchboard .	•	•	•	•	•	•	•	•		•		•	•	•	25
Total resista	nce	_			_			_				_		_	732

## CAPACITY.

Line of No. 18 Cable of No. 1							•	,	•						•	
Switchboard	•	•	•		•	•		•	•	•	•	•	•	•		.10
Total capac	ity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	2.71

Product of total resistance by total capacity =  $732 \times 2.71 = 1984$ .

If this line be reasonably free from extraneous noises, it will allow of good business conversation with Blake transmitters. If, however, it should be found to be a noisy line, we should have to return it by means of a similar and parallel line, making a metallic circuit, instead of through the earth.

It is evident that, by using a cable of lower capacity and resistance, we could have used a smaller pole wire, or, by choosing a larger pole wire, we could have used a cable of greater resistance and capacity.

It is also evident that our formula enables us to say which of these alterations will give us the desired ease of conversation at the minimum expense.

## IX.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

## ON TRIBROMTRINITROBENZOL.

By C. LORING JACKSON AND JOHN F. WING.

Presented June 15, 1887.

THE following paper contains the description of the first results of a research on tribromtrinitrobenzol and its derivatives, which we are obliged to publish now, as on account of the departure of one of us from Cambridge we cannot go on with the work together. Had it not been for this, we should have postponed its publication until our experiments on the reduction of triamidotrinitrobenzol had led to some definite result. At present we are able to describe only the tribromtrinitrobenzol, triamidotrinitrobenzol, and trianilidotrinitrobenzol, with several preliminary experiments on other substances, which we mention in order to reserve the further study of this subject for one of us, who will continue it in this laboratory.

The tribromtrinitrobenzol has never been described, for although Koerner \* in 1874 stated that he had obtained it by the action of a mixture of boiling fuming nitric and sulphuric acids on tribromdinitrobenzol, he gave no description of it, saying that this must be postponed till a later paper. Some years afterward (in 1879) Wurster and Beran,† after many attempts to prepare the substance according to Koerner, came to the conclusion that it could not be made in this way, as, even when Koerner's mixture of acids was heated with tribromdinitrobenzol to 220° in a sealed tube, they got only a very small amount of a substance melting from 200° to 220°, the greater part of the product being unaltered tribromdinitrobenzol. As this paper has remained unanswered by Koerner up to the present time, that is, for eight years, we have assumed that he has abandoned the subject, and have accordingly taken it up, our attention being called to it by the results obtained in the study of the action of nitric acid on



<sup>•</sup> Gazz. Chim., 1874, p. 425.

<sup>†</sup> Ber. d. ch. G., 1879, p. 1821.

trichlorbenzol described in a previous paper.\* Upon treating symmetrical tribrombenzol with a mixture of fuming sulphuric acid and a nitric acid of specific gravity 1.51, but essentially free from nitrous fumes, we found, as stated in the paper just mentioned, that tribromtrinitrobenzol was formed, thus confirming the results of Koerner, in opposition to those of Wurster and Beran; and in the same place we have tried to show that the most probable cause of the failure of these latter chemists to obtain tribromtrinitrobenzol was the presence of a large quantity of nitrous fumes in the nitric acid used by them, which raised its specific gravity without increasing its strength.

## Tribromtrinitrobenzol, C<sub>e</sub>Br<sub>s</sub>(NO<sub>2</sub>)<sub>3</sub>.

Symmetrical tribrombenzol (melting point 119°) was converted into tribromdinitrobenzol, either by treatment with nitric acid t of specific gravity 1.51, the mixture being warmed to secure complete action, or by boiling it with a mixture of commercial fuming nitric acid and common sulphuric acid. To convert the tribromdinitrobenzol, by whichever process prepared, into tribromtrinitrobenzol, 20 grm. of it were dissolved by the aid of heat in a mixture of about 500 c.c. of the nitric acid of specific gravity 1.51 mentioned above with one third of its volume of fuming sulphuric acid, since these proportions had been found by experiment to give the best result with the least consumption of acid, and the solution boiled gently in a flask loosely closed with a glass bulb. As a portion of the nitric acid volatilizes during the boiling, a little of the solid separates, which can be dissolved by the addition of more nitric acid, but this precaution is not necessary in working on a lage scale. When the mixture had boiled for four to five hours, it was allowed to cool, and then, disregarding the comparatively large am unt of solid which had separated, poured into snow, and the precipitate washed thoroughly with water and afterward purified, - first by extraction with hot alcohol, which removed the unaltered tribromdinitrobenzol, since the tribromtrinitrobenzol is but slightly soluble even in hot alcohol, - and then by crystallization from chloroform, which separated the less soluble tribromtrinitrobenzol from the tetrabromdinitrobenzol ‡ which was always formed at



<sup>\*</sup> These Proceedings, vol. xxii. p. 872.

<sup>†</sup> Prepared directly from sulphuric acid and nitre, not pushing the reaction beyond the formation of acid potassic sulphate. See our previous paper, these Proceedings, vol. xxii. p. 372.

<sup>†</sup> The purification and identification of this substance are described at the end of this paper. If the tribromtrinitrobenzol is to be used in making triami-

the same time. The crystallization from chloroform was continued until the substance showed the constant melting point of 285°; it was then dried at 100°, and its composition determined by the following analyses.\*

- 0.2310 grm. of the substance gave 19.6 c.c. of nitrogen under a pressure of 765 mm. and a temperature of 21°.
- II. 0.1688 grm. of the substance gave, according to the method of Carius, 0.2128 grm. of argentic bromide.

	Calculated for	Fou	
	C <sub>0</sub> Br <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> .	I.	IL.
Nitrogen	9.33	9.72	
Bromine	53.33		53.64

The yield was far from satisfactory, amounting on the average from about 15 to 20 per cent of the theoretical, although on one occasion we obtained 40 per cent. As, however, the tribromdinitrobenzol used in this case was the residue from the alcoholic extracts derived from previous preparations, we think that a considerable part of this large yield consisted of tribromtrinitrobenzol from the previous processes, which had been dissolved by the hot alcohol, since, although nearly insoluble in hot alcohol, it is not completely so. It follows from this that it is well to use the tribromdinitrobenzol obtained in purifying the crude product with alcohol as material for a new preparation.

Properties. — The tribromtrinitrobenzol forms good-sized, well-developed white crystals, with perhaps a slight yellowish tinge, which differ in habit according to the solvent from which they have been crystallized. From benzol, hexagonal prisms terminated by hexagonal pyramids are deposited, which look very much like some forms of quartz crystal; from a mixture of benzol and alcohol, long, slender, tapering prisms are obtained, which under the microscope seem to be made up of rows of hexagonal pyramids united as in cap quartz, so that the edges of the prisms are bluntly serrated; crystallized from chloroform, the prisms are not so slender as from benzol and alcohol, and the twinning just described is much better marked. These crystals, furrowed by numerous re-entering angles parallel to the basal plane, are very characteristic. The substance melts at 285° (uncorr.), and sublimes to a slight extent when heated in an air-bath, even at as

dotrinitrobenzol, it is not necessary to purify it completely from tetrabromdinitrobenzol. See page 143.

<sup>\*</sup> See also page 142.

low a temperature as 175°. It is but slightly soluble in alcohol, even when boiling, essentially insoluble in it when cold, soluble in chloroform, and more easily in ether, benzol, acetone, glacial acetic acid, or carbonic disulphide. Chloroform, or a mixture of benzol and alcohol, is the best solvent for it.

The tribromtrinitrobenzol is a decidedly reactive substance, forming compounds with most of the common reagents; of these compounds we have been able to study thoroughly only those derived from alcoholic ammonia and aniline, which will be described later in the paper. but some preliminary experiments with other reagents may find a place here. With potassic hydrate, dissolved in alcohol, a yellow product was formed which gave red potassium and vellow barium salts, the latter being only slightly soluble, and separating in hair-like crystals from its hot aqueous solution. It is probable that this product is the trinitrophloroglucin of Benedikt,\* but to decide this point the experiment must be repeated with a larger quantity of substance. With sodic ethylate it gives what appears to be a new compound. When boiled with an alcoholic solution of potassic sulphocyanate, it forms a dark red powder, which we have not yet succeeded in obtaining in crystals. When heated in a sealed tube with potassic iodide and alcohol to 150° for 18 hours, a crystalline compound is formed, which has a very high melting point and explodes when heated to a somewhat higher temperature; but the yield is so small that we have not been able as yet to obtain enough of it sufficiently pure for analy-All these substances will be more thoroughly studied in this laboratory, and the behavior of tribromtrinitrobenzol with other reagents, especially sodium malonic ester, will be investigated also. When tribromtrinitrobenzol is heated to 100° with common strong sulphuric acid, it dissolves, but crystallizes out unaltered as the solution cools. A boiling solution of argentic nitrate in alcohol has no action on it, and the same remark applies to argentic nitrite, as was to be expected. We hope, however, that the triiodtrinitrobenzol may react with this latter substance, and it was for this reason that we undertook the study of the action of potassic iodide on the tribromtrinitrobenzol.

In the hope of obtaining addition-products similar to those formed by Hepp's trinitrobenzol with hydrocarbons, we have studied the action of tribromtrinitrobenzol on naphthaline. For this purpose benzol solutions of the two substances were mixed in the proportion of one

<sup>\*</sup> Ber. d. ch. G., xi. 1876.

molecule of each, but we obtained from the mixed solutions only crystals melting at 285°; as, however, the melting-tubes contained a slight sublimate, and the habit of the crystals was somewhat different from that of tribromtrinitrobenzol, we thought it possible, although not probable, that a compound might have been formed, which decomposed before it melted, and have accordingly analyzed the crystals, which, remembering the instability of Hepp's substance, were dried only by pressing between filter-paper, in order to be certain that the substance should not be decomposed.

0.1200 grm. of the substance gave, according to the method of Carius, 0.1500 grm. of argentic bromide.

	Calculated for C <sub>6</sub> Br <sub>3</sub> (NO <sub>2</sub> ) <sub>3</sub> .	Found.	Calculated for $C_6Br_3(NO_2)_3C_{10}H_6$ .
Bromine	53.33	53.20	41.52

It is evident, therefore, that the substance is only tribromtrinitrobenzol, and that it does not combine with naphthaline under these conditions. The same negative result was obtained when chloroform or ether was substituted for benzol as the solvent. We may add, too, that the tribromtrinitrobenzol shows no tendency to unite with benzol, so far as we could find.

## Triamidotrinitrobenzol, C<sub>6</sub>(NH<sub>2</sub>)<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>.

When tribromtrinitrobenzol is mixed with cold alcoholic ammonia, an action sets in almost immediately, as shown by the appearance of an orange color in the solution; and, if the substances are allowed to stand for twelve hours in a corked flask at ordinary temperatures, the reaction proceeds further, but is not complete, as is shown by the presence of white specks consisting of unaltered tribromtrinitrobenzol in the undissolved solid. It is necessary, therefore, in order to bring this small amount of unaltered substance into the reaction, to boil the mixture in a flask with a return condenser for about half an hour, adding more alcoholic ammonia as it is needed. The nearly insoluble triamidotrinitrobenzol is then filtered hot from the orange liquid, which has the color of a strong solution of potassic dichromate,\* and the paler yellow solid purified by washing, first with water to remove ammonic bromide, and afterward with alcohol to get rid of the organic impurities.



Our study of the substances contained in this liquid is not complete as yet, but a description of the results obtained up to this time will be found on page 145.

The triamidotrinitrobenzol can be made conveniently also from the mixture of tribromtrinitrobenzol and tetrabromdinitrobenzol obtained in purifying tribromtrinitrobenzol, thus utilizing directly a secondary product, which could be separated into its pure constituents only with a great outlay of time and work. For this purpose, the mixture is treated with alcoholic ammonia in the manner already described when speaking of the preparation from pure tribromtrinitrobenzol, and the product freed from the tetrabromdinitrobenzol, which is not attacked by alcoholic ammonia under these conditions, by boiling and washing with benzol or chloroform after the washing with alcohol.

The composition of the substance after being dried at 100° was determined by the following analyses.

- 0.2352 grm. of the substance gave on combustion 0.2370 grm. of carbonic dioxide and 0.0544 grm. of water.
- II. 0.2346 grm. of the substance gave 0.2342 grm. of carbonic dioxide.\*
- III. 0.2186 grm. of the substance gave 60.4 c.c. of nitrogen under a pressure of 770 mm. and a temperature of 19°.
- IV. 0.1058 grm. of the substance gave 29.6 c.c. of nitrogen under a pressure of 765 mm. and a temperature of 20°.

•	Calculated for		Found	•	
	C <sub>6</sub> (NH <sub>2</sub> ) <sub>3</sub> (NO <sub>2</sub> ) <sub>3</sub> .	L	II.	ш.	IV.
Carbon	27.90	27.48	27.23		
Hydrogen	2.32	2.57			
Nitrogen	32.55			32.19	32.22

Properties.— As obtained from the action of alcoholic ammonia on the tribromtrinitrobenzol, the triamidotrinitrobenzol forms an amorphous powder of an orange or yellow color, according to the conditions under which it was prepared; crystallized from aniline or nitrobenzol, it forms small rhombic plates of a pale yellow color. It decomposes without melting above the boiling point of mercury, and is nearly, although not completely, insoluble in water, alcohol, ether, benzol, chloroform, or glacial acetic acid. It dissolves in aniline, or in nitrobenzol, and, as already stated, can be obtained in crystals from these solutions. Cold strong sulphuric acid slowly dissolves it, forming a pale yellow solution, but on dilution the unaltered substance is precipitated. Dilute sulphuric acid, or dilute or strong nitric or hydrochloric acid, has no action on it, and when the substance was suspended in alcohol

<sup>\*</sup> The hydrogen of this analysis was lost.

and hydrochloric acid gas passed into the liquid no change was observed. It is therefore either incapable of forming salts, or can form them only under unusual conditions. When the solution in strong sulphuric acid was heated it became charred.

We have made many attempts to convert the triamidotrinitrobenzol into an acet-compound, but have found that it was not acted on by glacial acetic acid, acetylchloride, or acetic anhydride, even when sealed with the substance, and heated to 150°; we infer, therefore, that the radical acetyl cannot be introduced directly into the molecule.

The reduction of triamidotrinitrobenzol naturally has engaged our attention, as by this means it might be possible to obtain hexamidobenzol. Owing to want of material, however, our experiments on this subject have not been brought to a conclusion, but we think it best to describe them briefly now, as we shall have no other opportunity to put them in print, if the future work of one of us on this subject should not lead to the desired result; and there seems to be only too much reason to fear that this will be the case, especially since Nietzki and Hagenbach \* have found that ammonia is eliminated in reductions which should lead to pentamidobenzol. Up to this time we have tried only three reducing agents, tin and hydrochloric acid, ammonic sulphydrate in alcoholic solution, and zinc dust and acetic acid. The first of these, tin and hydrochloric acid, removed ammonia from the molecule, as was proved by the formation of pink salt and the precipitation of ammonic chlorplatinate on adding chlorplatinic acid, the latter being analyzed for still greater certainty. This was the result whether tin and hydrochloric acid or stannous chloride and hydrochloric acid were used. The alcoholic solution of ammonic sulphydrate gave a more promising result; but, as it was evident that the product was decomposed at a temperature a little above that at which it was formed, we turned our attention to the third method, which seemed on the whole the most promising, since zinc dust and 80 per cent acetic acid acting in an atmosphere of carbonic dioxide seem to reduce the triamidotrinitrobenzol completely; at any rate, the yellow color disappears, and the whole goes into solution. This solution, after being freed from zinc with sulphuretted hydrogen, gave no precipitate with sodic hydrate, nor did ether extract anything from the alkaline It was blackened by exposure to the air even more readily than a solution of a salt of diamidobenzol, and the residue from it was decomposed easily by heat; chlorplatinic acid gave no precipitate with

<sup>\*</sup> Ber. d. ch. G., 1887, p. 831. See also p. 2114.

it, but chlorauric acid threw down an uninviting precipitate, which we thought was in part at least a product of oxidation. If the substance formed was really hexamidobenzol, it is evident that its isolation in a form fit for analysis will be a matter of great difficulty owing to its extreme instability. The study of this subject will be continued in this laboratory, however, as soon as a sufficient quantity of material can be prepared, and the work will be extended also to the action of other reducing agents, including those which form azo-compounds.

As yet we have been unable to finish the study of the substances contained in the orange-red filtrate formed in the preparation of the triamidotrinitrobenzol, because in spite of its marked color the amount of solid dissolved in it is far from large. It seems, however, to contain at least two compounds, one crystallizing in red needles, frequently grouped in round masses like chestnut burs, the other a yellow substance forming flat crystals; but the separation of these two bodies is a matter of such great difficulty that we have not yet succeeded in obtaining either of them in a state of purity, nor are we certain that these are the only secondary products of the reaction.

## Trianilidotrinitrobenzol, C6(NHC6H3)3(NO2)8.

This substance was prepared by allowing a mixture of tribromtrinitrobenzol and aniline, in the proportion of one molecule of the former to six of the base, to stand at ordinary temperatures, when the reaction runs slowly, but is complete after the mixture has stood for a day or two. The product was purified by washing with water, to which a little hydrochloric acid was added to remove any slight excess of free aniline, and crystallizing the residue from a mixture of alcohol and chloroform. It was dried at 100°, and analyzed with the following results.

- I. 0.1468 grm. of the substance gave on combustion 0.3176 grm. of carbonic dioxide and 0.0516 grm. of water.
- II. 0.1830 grm. of the substance gave 28.1 c.c. of nitrogen at 25° temperature and 755 mm. pressure.

	Calculated for	Fou	nd.
	C <sub>6</sub> (NHC <sub>6</sub> H <sub>5</sub> ) <sub>5</sub> (NO <sub>2</sub> ) <sub>5</sub> .	I.	IL.
Carbon	59.26	58.99	
Hydrogen	3.71	3.90	
Nitrogen	17.28		17.02

If an excess of aniline is used in the preparation, and the mixture heated, a coloring matter is formed looking like rosaniline; but the VOL. XXIII. (N. S. XV.)

purification of this substance was attended with such great difficulties that we have abandoned for the present the further study of this reaction, in which the nitro groups undoubtedly play a part.

Properties. — The trianilidotrinitrobenzol forms an orange powder, crystallizing from alcohol or chloroform in fine red needles, which melt at 238°. It is essentially insoluble in water, soluble with difficulty in alcohol, but easily in chloroform, soluble in ether, benzol, glacial acetic acid, or acetone. The best solvent for it is a mixture of alcohol and chloroform. Hydrochloric acid has no action on it, and in general it shows no more tendency to form salts than the corresponding amido compound. Strong nitric acid produces no change of color when added to it.

## Tetrabromdinitrobenzol, C<sub>6</sub>Br<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>.

As has been already stated, during the preparation of the tribromtrinitrobenzol from tribromdinitrobenzol by the action of nitric acid and fuming sulphuric acid there was formed invariably another substance which melted in the crude state at about 230°, and was left behind with the tribromtrinitrobenzol after the tribromdinitrobenzol was removed with alcohol, and was separated partially from it by crystallizing the residue from chloroform, in which the trinitro compound is less soluble than the other substance. In this way it is easy to get the trinitro compound in a state of purity; but to purify completely the other substance it is necessary to submit the residue from the evaporation of the chloroform mother-liquors to systematic fractional crystallization from a mixture of alcohol and benzol, which removes a small quantity of tribromtrinitrobenzol. These crystallizations lowered the melting point instead of raising it, as is usual, and after it had been brought down from about 230° to 224° it remained constant, and then the substance, dried at 100°, was analyzed with the following results.

- I. 0.3526 grm. of the substance gave 18.7 c.c. of nitrogen at 24° temperature and 764 mm. pressure.
- II. 0.1690 grm. of the substance gave, by the method of Carius, 0.2606 grm. of argentic bromide.

•	Calculated for	Fo	and.
	C <sub>6</sub> Br <sub>6</sub> (NO <sub>2</sub> ) <sub>3</sub> .	I.	п.
Nitrogen	5.78	5.97	
Bromine	66.11		65.62

These analyses and the melting point 224° prove that the substance is the tetrabromdinitrobenzol melting point 227-228°, discovered by Von Richter.\*

The following experiments were tried to throw light upon the manner in which the tetrabromdinitrobenzol was formed. In the first place, to prove that it was not formed from an impurity (tetrabrombenzol) in our tribrombenzol, we have prepared it from an analyzed sample of tribromdinitrobenzol. This experiment was hardly necessary, as the tribrombenzol and tribromdinitrobenzol used by us in working on the large scale showed the correct melting points within two degrees; but we felt that absolute certainty on this point was important, and accordingly prepared some perfectly pure tribromdinitrobenzol, melting point 190° (Von Richter† gives 191°, Koerner‡ 192°), which gave on analysis the following result.

0.1658 grm. of the substance gave, according to the method of Carius, 0.2314 grm. of argentic bromide.

	Calculated for CaBr <sub>s</sub> (NO <sub>2</sub> ) <sub>2</sub> H.	Found.
Bromine	59.26	59.39

This was treated with a mixture of nitric acid and fuming sulphuric acid, precisely as in the preparation of tribromtrinitrobenzol, and yielded a product which, after removing the unattacked tribromdinitrobenzol, consisted of tribromtrinitrobenzol and tetrabromdinitrobenzol in about equal parts, thus proving that the tetrabromdinitrobenzol is not derived from an impurity, but is formed during the process.

A second experiment had for its object to determine whether the conversion of the tribromdinitrobenzol into tetrabromdinitrobenzol was due to the fuming sulphuric acid, which might well be the case, since Bässmann § has observed that symmetrical tribrombenzol is converted in part into pentabrombenzol, when heated with fuming sulphuric acid to 100° from a week to a fortnight. We accordingly heated another quantity of the pure tribromdinitrobenzol with an excess of fuming sulphuric acid in a sealed tube to 100° for twelve hours, but no tetrabromdinitrobenzol was formed, and, as the temperature of our mixture during the manufacture of the tribromtrinitrobenzol could have been little, if at all, above 100°, and that process was carried on for only five hours, we are inclined to ascribe the formation of the tetrabrom compound to the nitric rather than the sulphuric acid.

<sup>•</sup> Ber. d. ch. G., 1875, p. 1427.

<sup>†</sup> Ber. d. ch. G., 1875, p. 1426.

<sup>#</sup> Gazz. Chim., 1874, p. 425.

<sup>§</sup> Ann. Chem., cxci. 208.

In a third experiment the mixture of tribromdinitrobenzol with nitric and fuming sulphuric acids was boiled for only a quarter of an hour, instead of for the usual five hours, and the proportion of tetrabromdinitrobenzol formed was comparatively small, it would seem, therefore, that it is formed chiefly in the later part of the boiling; but it is not advantageous in preparing tribromtrinitrobenzol to diminish the length of the boiling, as the superior purity of the product does not compensate for the much smaller yield. We may add, that another experiment showed that it was impossible to convert tribromtrinitrobenzol into tetrabromdinitrobenzol by boiling it with the mixture of nitric acid and fuming sulphuric acid.

Von Richter, the discoverer of tetrabromdinitrobenzol, gave the melting point 227-228°, whereas our substance showed a constant melting point of 224°. We are of the opinion, however, that Von Richter's melting point is more correct than ours, as it might well be that a small quantity of tribromtrinitrobenzol, sufficient to lower the melting-point 4°, could not be removed by crystallization, and in fact our analysis seems to indicate the presence of such an impurity; but as our object was to identify the substance rather than study its properties, we did not think it worth while to sacrifice the large amount of time and labor which would undoubtedly have been necessary to settle this point thoroughly. Von Richter also states that it is soluble in alcohol or benzol, and Bodewig \* has published a thorough description of its crystalline form. The following properties, which we have had occasion to study, have not been published heretoforé, so far as we can find. It begins to sublime at about 175°, and is soluble in methylalcohol, ether, acetone, glacial acetic acid, or carbonic disulphide; the best solvent for it is a mixture of alcohol and benzol, in the former of which it is but sparingly soluble. It dissolves in cold sulphuric acid, but is precipitated unchanged on dilution. over a free flame with sulphuric acid, it is destroyed. The bromine in it is much more firmly attached to the molecule than in the tribromtrinitrobenzol, as it is not removed when the substance is boiled with alcoholic ammonia in open vessels. It is also very hard to effect its complete decomposition in its analysis according to Carius.

Finally, we may remark that it is highly probable that the substance melting above 200° obtained by Wurster and Beran by heating tribromdinitrobenzol to 220° in a sealed tube with a mixture of fuming nitric and sulphuric acids was the tetrabromdinitrobenzol.

<sup>\*</sup> Zeitschr. Kryst., iii. 398.

## X.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE. — J. P. COOKE, Director.

# THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.

By Josiah Parsons Cooke

AND

THEODORE WILLIAM RICHARDS.

Presented June 15, 1887.

#### INTRODUCTION.

SINCE the application by Dalton of the atomic theory to explain the definiteness of the combining proportions of the elementary substances of chemistry, these proportions have been generally regarded as the ratios of the weights of the atoms, and the values assigned to each element have been generally called atomic weights.

The conception was early suggested and advocated by Dr. Prout, an eminent physician of London during the first half of this century, that the elementary atoms were all aggregates of the atom of hydrogen, the lightest atom known. If this were true, it would of course follow that the atomic weights of the elements would all be multiples of the atomic weight of hydrogen; so that, if the weight of the atom of hydrogen were selected as the unit of the system, all other atomic weights must be multiples of this unit, and therefore whole numbers.

The facts known at the time (1815) were not inconsistent with this view; but as the methods of chemical analysis were improved, and the combining proportions determined with greater accuracy, marked discrepancies from Prout's hypothesis appeared. Still, so great was the hold which the conception had taken upon chemical students, that for a long time the nearest whole numbers to the combining proportions observed were accredited as the true value of the atomic weights, rather than the actual mean of the experimental results; and this practice is still followed in many standard publications, notably the "Jahresbericht

uber die Fortschritte der Chemie." In many cases the observed values were so near whole numbers that no important error in the calculation of analyses arose from this practice, the differences neglected being no greater than the uncertainties of analytical method, and this was especially true with regard to the larger atomic weights.

One exception to the theory, however, was so marked that it could not be overlooked, namely, the atomic weight of chlorine, which was capable of being determined with great accuracy; and all the determinations uniformly gave a result which was closely 35.5. This and a few similar cases suggested the idea, that, if the atomic weights were not even multiples of the received hydrogen atom, they might be multiples of the half or quarter hydrogen atom, which would simply amount to taking as the ultimate atom of material things a still smaller unit.

The well-known chemist, Dumas of Paris, was led by this view to undertake a redetermination of a large number of atomic weights, and many of the results then obtained are still accepted as authoritative. As was to be expected, Dumas found a much closer agreement with this modified theory than with the original hypothesis of Prout; but obviously such evidence could have but little bearing on the general theory that the atoms were all aggregates of some common unit, for by taking that unit small enough, — even no smaller than the one hundredth of the received hydrogen atom, — all the atomic weights, even those most accurately determined, would be expressed by whole numbers within the limits of probable error.

Soon after, Stas of Brussels, a former assistant of Dumas, endeavored to set the question of Prout's theory at rest by an investigation which will be ever memorable for its extreme accuracy.† He selected for his investigation those elements whose combining proportions were capable of being determined with the greatest accuracy, and, working on large quantities of material, with every refinement which a full knowledge of analytical methods could suggest, he obtained results which it seemed impossible to reconcile with the theory in any way. This investigation, published in 1865, seemed at first to disprove the theory altogether.

Nevertheless, when Stas's results came to be collated, and as other determinations of similar accuracy came to be published, the fact appeared that a large number of the most accurately determined atomic

<sup>\*</sup> Annales de Chimie et de Physique, 8d ser., lv. 129 (1859).

<sup>†</sup> Mémoires de l'Académie Royale de Belgique, xxxv. Also Ann. Ch. Pharm., Suppl., iv. 168.

weights stood to each other in the relation of whole numbers within the limits of accuracy of the most refined experimental work. The number of these cases was so large that it seemed highly improbable that the coincidences should be the result of chance.

This idea was prominently set forth by Professor Mallet of the University of Virginia, in his admirable paper on the Atomic Weight of Aluminum,\* which was a striking illustration in point; and the same feature was also made prominent by Professor F. W. Clarke of Washington, after a careful review of all the determinations of atomic weights.†

The coincidences appear more striking if the values of the weights referred to are given in values of the oxygen atom assumed to be 16, as has been done by Professor George F. Becker in his digest of atomic weight determinations.‡ The following table from the writer's work on Chemical Philosophy will make clear the point in question.

#### ATOMIC WEIGHTS

#### MOST ACCURATELY DETERMINED.

Hydrogen						1.002	Chlorine .					85.46
Lithium .						7.01	Potassium					89.14
Carbon .					•	12.00	Calcium .					40.00
Nitrogen .						14.04	Bromine .				•	79.94
Oxygen .		•				16.00	Silver					107.93
							Antimony					
Sodium .					•	23.05	Iodine					126.85
Magnesium						24.00	Barium .					137.14
Phosphorus						81.05	Thallium .				•	204.11
Sulphur .			•	•	•	<b>32.07</b>	Lead					206.91

This table includes all the atomic weights which up to 1882 could be regarded as known within one thousandth of their value, and with one or two notable exceptions there is no instance in which the value differs from a whole number by a quantity greater than the possible error, though not always the "probable error," of the processes employed in their determination.

Were these numbers wholly independent of each other and distributed by no law, we should expect to find every possible intermediate value, and the fact that they so nearly approach whole numbers can-

<sup>\*</sup> Phil. Trans., 1880, p. 1003.

<sup>†</sup> Smithson. Misc. Coll.; Constants of Nature, Part V. p. 270.

<sup>#</sup> Smithson. Misc. Coll.; Constants of Nature, Part IV.

not fail to produce on the mind the impression that there is some influence which tends to bring about this result.

It may be that the discrepancies are due to unknown constant errors, which every experimentalist knows are greatly to be feared. Or it may be that there is in nature a tendency to whole multiples; and this last view, if not compatible with our present conception of the atomic theory, may hereafter appear as one of the phases of a broader philosophy.

The force of evidence which such a distribution of values as the above table presents was brought home to the writer in his investigation of the atomic weight of antimony. After eliminating various causes of error, he was enabled to determine with great accuracy the atomic weights of antimony, silver, and bromine, in one and the same series of experiments; and it appeared that this ratio was

with a probable error of less than one in the last decimal place. Here then is a ratio of whole numbers within the one hundredth of a single unit. Since the ratio of the atomic weights of silver and oxygen have been determined with great accuracy, we can extend the above proportion to a fourth term, the atomic weight of oxygen, which appears also as a whole number, perhaps with a somewhat larger probable error. Still, we have not reached the unit of the system, and when we attempt to extend the ratio to the atomic weight of hydrogen, we find that the most probable value from all experiments hitherto made gives the ratio not of 16 to 1, but of 16 to 1.0025.

If now we wished to refer to the hydrogen unit the atomic weights of antimony, silver, bromine, and oxygen whose ratios of whole numbers had been determined as above, it was only necessary to divide all the terms of the above proportion by 1.0031, when we obtain the series of values given below the others, and all semblance to the hypothesis of Prout disappears, although of course the second series of numbers bear the same ratios to each other as the first:—

Antimony.	Silver.	Bromine.	Oxygen.	Hydrogen.
120.00	108.00	80.00	16.01	1.0031
119.60	107.66	79.75	15.96	1.00

The numbers in the lower of the two proportions appear as uncommensurable as Stas maintained that they were, and the same is true

Additional Experiments on the Atomic Weight of Antimony, Am. Acad. Proc., vol. xvii. p. 13, by Josiah Parsons Cooke.

of most of the atomic weights, when given, as is usual in recent textbooks, on the basis of the hydrogen unit.

When as the result of his investigation on the atomic weight of antimony there was presented to the writer the ratios of whole numbers as shown in the first of the above proportions, with the single exception of the atomic weight of hydrogen, the question was at once suggested: Is the ratio of the atomic weights of oxygen and hydrogen in fact that of 16:1.0025, as the general average of all trustworthy determinations hitherto made seems to indicate, or was there some constant error lurking in these results which caused the very slight variation from 16 to 1 required by the theory? In looking at the proportion thus displayed, it seemed as if the variation from the theory must be apparent, and he determined to ferret out the hidden error if possible. This investigation was undertaken in the autumn of 1883, but owing to the condition of the writer's sight the work has been greatly delayed.

No one can study the record of the investigations by which the ratio of the weights of the oxygen and hydrogen atoms have been determined, without receiving the impression that they are by no means decisive in regard to the theory we are discussing, and it is also equally evident that this ratio, if it could be fixed beyond doubt, would be a crucial test of the theory.

## PREVIOUS WORK.

The methods by which the atomic weights of oxygen and hydrogen have been determined may be divided into two classes; first, the direct method of determining the ratio in which the proportions of oxygen and hydrogen uniting to form water were actually weighed; secondly, the confirmatory method, to whose results small weight could be given independent of the first.

Among confirmatory methods we must unquestionably class the classical determinations by Regnault of the density of oxygen and hydrogen gases under normal conditions at Paris; that is, in so far as these determinations bear on the question of the ratio of the atomic weights.

According to the molecular theory the ratio of the densities of oxygen and hydrogen gases could only be the ratio of their molecular or of their atomic weights when both materials were in the condition of perfect gases, of which condition the test would be an exact conformity to Mariotte's law. Now, as Regnault himself elegantly demonstrated, oxygen and hydrogen gases at the standard conditions of temperature

and pressure not only do not exactly obey Mariotte's law, but the deviations from the law in these two cases are in the opposite directions, oxygen gas being condensed by increasing pressure more, and hydrogen gas less, than the law requires. Hence theory would not lead us to expect that the ratio of the densities of these gases at the standard conditions would be the exact ratio of their atomic weights. But obviously it may be that this inference from the molecular theory is not legitimate, or it may be that the effect of the imperfect aeriform condition would not perceptibly influence the apparent atomic ratio; and hence the confirmation afforded by Regnault's results is of value.

In the same category we must class also the determination of the atomic weight of oxygen made by Thomsen of Copenhagen, who weighed the amount of water obtained by burning a measured volume of hydrogen gas. Here the reduction of the volume to weight involved a knowledge of values and conditions which could not be known with the greatest accuracy, and unfortunately the details of the experiments have not been published.

Again, we should class simply as confirmatory results deduced indirectly, and involving the values of other atomic weights, however accurately these subsidiary values may be supposed to be known; such, for example, as Stas's determination of the amount of chlorine in ammonic chloride.

Turning now to the actual direct determinations of the combining proportions of oxygen and hydrogen, there are only two which are of any present value. Of these by far the most important is the classical investigation of Dumas, "Researches on the Composition of Water." \* This is one of the most memorable investigations in the history of chemistry, and its general principles are known to every student of the science. An indefinite amount of hydrogen was burnt by means of cupric oxide; the amount of oxygen consumed was determined by the loss of weight of the combustion tube, and the amount of water formed was collected and weighed directly. The experiments were on a very large scale, the amount of water produced varying from 15 to 70 grams. The greatest care was taken to insure the purity of the materials used, every known experimental means was employed to secure accuracy, and all necessary corrections were applied to the results. Estimated on the system at present in use, the value of the atomic weight of oxygen obtained by Dumas as the mean of nineteen

Ann. de Chim. et de Physique, 3d ser., viii. 189 (1842).

determinations was 15.9607, with a probable error of  $\pm 0.0070$ , the highest value being 16.024, and the lowest 15.892.

The investigation of Erdmann and Marchand\* was far less extended, and some of the precautions taken by Dumas were neglected because deemed unnecessary. No pains seem to have been taken to obtain pure cupric oxide, and the material used in several of the determinations was described as "kaufliche Kupferglühspan," while that used in the others was obtained by igniting cupric nitrate; and no proof is adduced in either case of the purity of the material employed.

The results are divided into two groups, and in the experiments of the second group the air was exhausted from the combustion tube before weighing; but it appears from the paper that the marked difference between the two series of experiments depended rather on the character of the cupric oxide, and on varying conditions used, than on this circumstance. The first series of four results, when averaged, gave the value 15.937, with a probable error of  $\pm 0.0138$ , while the mean of the second series was 16.009, with a probable error of  $\pm 0.0030$ . The study of the paper, however, does not confirm the expectation that the results of the second series are more trustworthy; for the closer agreement and smaller probable error appear to be the result of the identity of conditions, which was maintained in this series, but not in the first. Judging from the paper, we should be inclined to place most reliance on the first series, in which the conditions of the experiments were varied, rather than on the second, which seems obviously to be influenced by some constant error.

The results, then, thus far obtained, are as follows: -

## Direct Determinations.

Dumas (	ninete	en determ	inations)	$15.9607 \pm 0.0070$
Erdmann	and	Marchand	(first four)	$15.9369 \pm 0.0138$
"	"	"	(second four)	$16.0095 \pm 0.0030$

## Confirmatory Determinations.

Dumas and Boussingalt † (gas densities)	$15.954 \pm 0.031$
Regnault ‡ (gas densities)	$15.961 \pm 0.0044$
Thomsen § (not fully described)	15.960

Journ. f. Prakt. Chem., 1842, vol. xxvi. p. 461.

<sup>†</sup> Compt. Rend., xii. 1005; also Constants of Nature, Part V. p. 6.

t Compt. Rend., xx. 975; also Constants of Nature, Part V. p. 6.

<sup>§</sup> Berichte der deutsch. Chem. Gesell., 1870, p. 928; also Constants of Nature, Part V. p. 8.

The one process by which the relative combining proportions of oxygen and hydrogen have been hitherto directly determined is open to serious criticism. In the first place, the circumstance that the weight of the hydrogen is eight times smaller than that of the oxygen, and that this weight has only been estimated by difference, is excoedingly unfavorable to the accuracy of the process. It can easily be seen, that, in order to establish a ratio like 1 to 8, the highest accuracy demands that each term of the proportion should be known to an equal degree of exactness. Thus if in a given experiment we have 8 grams of oxygen uniting with 1 gram of hydrogen, it is of no avail to weigh the oxygen to the tenth of a milligram, unless we can weigh the hydrogen to the same proportionate degree of accuracy. For an error of eight tenths of a milligram in the weight of the oxygen, or an error of nine tenths of a milligram in the weight of the water, will have no more influence on the ratio we are seeking than an error of one tenth of a milligram in the weight of the hydrogen. Now, in the process we are discussing the weight of the water can be determined to within a few tenths of a milligram; that is, with all the accuracy with which our problem requires that the larger term of the proportion 8 to 1 should be known. It is quite different with the weight of the oxygen. This last is found by weighing the glass combustion tube containing cupric oxide before and after the experiment, and between the two weighings the tube is heated to a low red heat for several hours while a stream of hydrogen gas is passing through it; and there are several causes which may lead to the variation of these weights, independent of the oxygen which has been used up in the process. We shall allude to some of these causes below, but their effect would be comparatively unimportant if they only led to a small error in the observed weight of the oxygen. Unfortunately their effect is not thus limited; for when, in order to find the weight of the hydrogen, we subtract from the weight of the water, which may be regarded relatively as accurately known, the weight of the oxygen, which may be for the causes referred to slightly erroneous, the whole error appears in the weight of the hydrogen thus found, and in the opposite direction. If, for example, the weight of the oxygen is too large, the weight of the hydrogen will be too small by exactly the same amount; and although the error may be an inconsiderable part of the weight of the oxygen, it may be a very appreciable quantity in the weight of the hydrogen.

On the other hand, if a means could be devised for weighing the hydrogen, leaving the oxygen to be determined by subtracting this

smaller weight from the weight of the water, then a small error in the observed weight of the hydrogen would have no appreciable effect on the weight of the oxygen.

Dumas fully recognized the source of error to which we have referred, and in his paper on the subject wrote what may be translated as follows:—

"Of all analyses presented to a chemist, that of water is the one which offers the greatest uncertainty. Indeed, one part of hydrogen unites with eight parts of oxygen to form water, and nothing would be more exact than the analysis of water, if we could weigh the hydrogen as well as the water which results from its combustion. But the experiment is not possible under this form. We are obliged to weigh the water formed, and the oxygen which was consumed in producing it, and to determine by difference the weight of the hydrogen which has entered into combination. Thus an error of  $\frac{1}{8}$  in the weight of the oxygen, is equivalent to an arror of  $\frac{1}{8}$  or  $\frac{1}{9}$  in the weight of the hydrogen. Let these two errors be in the same direction, and the total error will amount to  $\frac{1}{8}$ ."

In the second place, however carefully the exterior surface of the combustion tube may be guarded, it is impossible that the contents of the tube should bear the same relations to the surrounding atmosphere before and after the combustion. We begin with a tube containing cupric oxide in different states, and we end with it containing reduced copper, whose condition will vary more or less with the character of the oxide employed; and the power of these materials to occlude air or hydrogen is an unknown quantity in our experiment. That it is an appreciable quantity is evident from several incidental observations.

Dumas endeavored to avoid any source of error arising from this cause by exhausting the combustion tube before weighing it, but he himself expresses a doubt whether a trace of hydrogen might not have been left. Erdmann and Marchand in part of their experiments resorted to the same expedient, but their results obviously vary with the condition of the cupric oxide employed; and the following remarks of Schutzenberger, in a discussion of the variability of the law of definite proportions before the Chemical Society of Paris in 1883, as quoted in the "American Journal of Science," 3d series, Vol. XXVI. page 65, have an important bearing on the same point:—

"When water is synthesized by reduction of a known weight of CuO, by weighing the reduced Cu and the water formed, it is found that the ratio of O to H is not constant, but varies with the state of division and of saturation of the oxide, the duration of contact of the water formed with the oxide, and with the temperature, from 7.95 to 8.15. The latter value is obtained with a saturated and divided oxide filling the tube, the former with oxide in lumps filling the tube for a space of 25 cm. With a larger empty space the ratio has fallen to 7.90. When the synthesis of water is effected by weighing the hydrogen consumed (as by dissolving a known weight of zinc in HCl) and the water formed, the ratio differs according to the contents of the combustion tubes. If it contains granular CuO of a length of 80 cm. heated to redness, the ratio O: H is 7.96 to 7.98 to 1; at a low temperature, 7.90 to 7.93; if the CuO is replaced by PbCrO<sub>4</sub>, from 7.89 to 7.93."

In addition to all this, impurities in the oxide of copper might have a serious influence on the result. As before said, Erdmann and Marchand speak of using "kaufliche Kupferglühspan"; but in our work we could find no commercial cupric oxide which did not contain a marked amount of arsenic. We examined a number of specimens coming from the best German and American dealers, and there was not a single instance in which we did not find arsenic, and even when the material was marked "purissimum." In some cases the amount of arsenic was so great, that, after successive reductions and oxidations, abundant crystals of arsenious oxide collected at the exit end of the combustion tube. It is unnecessary to add that the hydrogen used was free from all such impurity.

For our own experiments, of which the results are given below, not only was the oxide of copper prepared from absolutely pure electrolytic copper, but also, as will be shown, the combustion tube was left at the end of the determination as it was at first, and the same tube was used for a number of experiments.

#### APPARATUS FOR WEIGHING HYDROGEN.

In entering on a new investigation of the oxygen and hydrogen ratio, it was evident at the outset that no advantage was to be gained by multiplying determinations by the old method. The only hope of improvement lay in finding some method of weighing the hydrogen with sufficient accuracy; and it was essential to determine this weight to within one ten-thousandth, or at least one five-thousandth, of its value.

A gas can only be weighed by enclosing it in a glass globe, or some similar receiver, and hydrogen is so exceedingly light that its total

weight can only be a very small fraction of the weight of the containing vessel. Moreover, as the buoyancy of the air is fourteen and one half times as great as the weight of the hydrogen, the variations in buoyancy caused by changing atmospheric conditions have an all-important effect on the apparent weight. The late Professor Regnault, of Paris, devised, however, a very ingenious method of compensation. which could readily be applied in this case. It consisted in balancing the globe containing hydrogen, hung to one arm of the balance, by a second globe of exactly the same external volume and made of the same material, hung to the opposite arm; and so arranging the balance case that they should hang in the same enclosure, and therefore be equally affected by atmospheric changes. This method was applied in the problem before us; and after a number of trials it was found possible to make the compensation so accurate that under good conditions the weight of a globe holding five litres of gas did not vary more than one tenth of a milligram through large changes of temperature and pressure. In order now to weigh hydrogen with this apparatus, it was only necessary to exhaust the air from the glass receiver, and, after balancing it as described, to fill it with pure gas, when the increased weight -- less than half a gram with our apparatus --- was the weight of hydrogen required.

The balance employed was an excellent one, made about twenty years ago by Becker and Sons, of New York. With a load of five hundred grams in each pan, it turns very perceptibly with one tenth of a milligram, and shows this small difference of weight with very great constancy.

The globe and its counterpoise were hung from hooks soldered to the bottoms of the pans by means of wires which swung freely through small holes made for the purpose through the bottom of the balance case, and also through the top of the shelf on which the case stood. The enclosure in which the globe and its counterpoise hung was a box made of tinned iron fastened to the bottom of the shelf, and having doors in front like an oven, through which the globe could be removed or hung in position. This case was coated with lampblack on the inside, in order to secure uniformity of temperature; and the air was kept dry by means of two large dishes of sulphuric acid, placed on shelves at the top of the case. We first placed the sulphuric acid dishes on the bottom of the case in the usual way, but we found it impossible thus to secure a uniform condition of the atmosphere within; and as moist air is necessarily lighter than an equal volume of dry air at the same temperature and pressure, it is obvious that any drying material will have the

greatest efficiency when placed near the top of the space to be protected. The tin box was itself enclosed in a cupboard, but not otherwise protected; and the balance case was surrounded by curtains, in order to shield the beam from radiation.

With the apparatus so arranged, it was found possible to obtain most satisfactory and concordant results to tenths of a milligram when the change in the temperature of the balance-room was not very rapid; but any sudden changes produced by artificial heating would cause slight currents of air in the interior of the case, whose effect became very sensible, but whose influence we were able to eliminate. The best series of results, however, (the second series in the table below,) was obtained during the month of June, when there was no artificial heat in the building, and the temperature varied but little during day and night.

The globe used for holding the hydrogen — shown in Fig. 1 in about one sixth of its actual dimensions — has an interior capacity of 4961.5

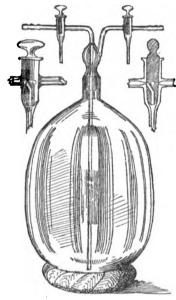


Fig. 1.

cubic centimeters, and weighs 570.5 grams. The cap with the connecting tubes was ground into the neck, and this joint, as also the stopcocks, was so carefully made that there was absolutely no leakage, and the globe would hold a vacuum indefinitely; as was shown frequently by its remaining hung on the balance for weeks together when exhausted without change of weight. The apparatus was made by Emil Greiner. of 79 Nassau Street, New York, whose careful workmanship greatly contributed to the success of our investigation. The details of the stopcock are shown at the sides; and it will be noticed that, besides the direct way, there is a side way through the plug of the stopcock independent of the first, by which,

when the stopcock is closed, a connection is established with the base of the cock, through which the gas may escape.

Assume now that the interior of the globe has been exhausted, and a gas current established through this side aperture from one of the generators employed. On turning the stopcock, the side aperture is first closed, and then the direct way slightly opened, so that all the gas evolved now passes into the globe; and it was found possible to regulate the current with such nicety as not to cause any sudden changes of tension in the generator, which was always provided with an overflow by means of which the tension could be watched, and according to which the stopcock was regulated.

The filling of the globe was one of the critical points of the determination. It generally occupied from one to two hours, and during all this time it was necessary, with the hand on the stopcock, carefully to watch the tension at the overflow already mentioned, and represented in Fig. 5, and Figs. 7 and 8 of Plate. From the beginning to the end of the operation there was a greater tension in the generator than in the outside air, by about one inch of mercury. When the connection was once established between the generator and the globe, there was absolutely no leakage through the side way, as was tested in several cases by dipping the mouth of the tube at the base of the cock under mercury.

The whole process of weighing the hydrogen was finally reduced to the following manipulation. The globe was connected by means of a rubber hose with a rotatory air-pump having automatic valves, made by E. S. Ritchie of Boston. It was then exhausted to within 1 mm. of mercury. Next, closing the cock and disconnecting the globe, it was cleaned with distilled water and fine cotton cloth; at least, this was done five or six times during the determinations. But as the globe when out of the balance case was always protected by a cylindrical tin box with a cover, from which the exit tubes projected, it was usually only necessary to clean the exit tubes in this careful manner, simply dusting off the globe with a large camel's-hair brush, before hanging it in the balance case. In this part of the operation it was necessary to take care not to communicate to the globe a charge of electricity by rubbing it with a perfectly dry cloth.

The globe was hung on a wire stirrup, which caught the exit tubes, as the glass joint was sufficiently strong to support the weight of the globe. The globe was so nearly balanced by its equipoise that when exhausted it only required about one decigram to establish equilibrium. The time required to attain perfect equilibrium varied with the conditions. If the glass had been previously cleaned as described above, perfect equilibrium might not be reached for forty-eight hours, or even longer, while if the glass had only been dusted, twelve hours were generally sufficient.

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After the tare had thus been taken, the globe was removed from the balance, placed in the protecting case, and filled with hydrogen as just described. The inlet tube, to which a rubber connector had been attached, was scrupulously cleaned as before, and the globe was again dusted and hung on the balance. During all these transfers the globe was always handled with clean cotton cloth, and the hands never came in contact with the glass. The increased weight was now the weight of the hydrogen; and as the volumes equipoised were exactly the same, and the additional weight was represented by less than five tenths of a gram of platinum, any correction for the buoyancy of the atmosphere is unessential.

#### COMBUSTION APPARATUS.

The apparatus by which the combustion of the hydrogen was made is represented in the Plate accompanying the paper (Fig. 6). It is made up of a series of small combustion furnaces, which are a modification of a kerosene-oil stove called "the American," very much used in the United States. This stove, as adapted to chemical uses by the writer,

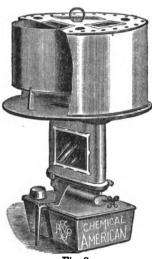


Fig. 2.

is shown in Figs. 2 and 3, and it has proved of great value, not only for elementary chemical experiments in school courses, where illuminating gas is not to be had, but also in a well equipped chemical laboratory. The stove is made for burning kerosene oil, but alcohol can also be burnt in it with decided advantage for chemical work. The figure of the stove has been drawn to about one sixth of the actual size.

In the figure of the combustion apparatus (Fig. 6, Plate) it will be noticed that the globe, protected by its case, stands about in the middle of the line. By means of a suction pump attached to the extreme right of the apparatus, a current of air is main-

tained through the whole length. Beginning now at the extreme left, the air first passes over reduced copper, and is deprived of its oxygen. It next passes over cupric oxide, by which any traces of hydrogen that had remained occluded by the reduced copper, or any traces of hydrocarbons in the air itself, are burnt. It next passes

through caustic potash bulbs, and then through a system of driers, meeting successively calcic chloride, sulphuric acid, and phosphoric

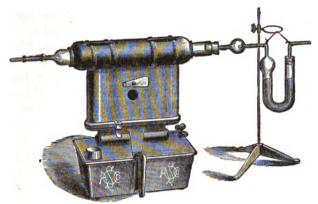


Fig. 8.

pentoxide. It now enters the globe through the inlet tube reaching to the bottom, carrying before it the hydrogen into the combustion furnace.

The water from the combustion was collected in a condenser, — the details of whose construction are represented in Fig. 4, — which was shielded from the furnace by a screen of asbestos paper. Nine tenths

of the water was condensed in the middle tube, and all but the last traces of the aqueous vapor were absorbed by the sulphuric acid through which the air subsequently bubbled up at the bend of the U tube, between glass beads, which broke the ascent and divided the bubbles. With this condenser was connected a U tube containing phosphoric pentoxide, which absorbed the last traces of the aqueous vapor, seldom, however, gaining in weight more than two milligrams during a combustion lasting from seven to eight hours. Then follows a safety tube containing calcic chloride (or in some cases phosphoric pentoxide), to prevent any reflex diffusion, and finally an adaptation of the principle of Mariotte's flask to regulate the velocity of the air



Fig. 4.

current. It will be seen that the open mouth of the central tube of this last apparatus dips under the mercury in the tall jar, so that by raising or lowering it the strength of the current could be exactly regulated. Before beginning a combustion, the place of the hydrogen globe was supplied by a straight piece of glass tubing, and the air current maintained through the heated combustion tube until the cupric oxide was perfectly dry. Next the furnace at the extreme left was lighted, and the current continued until the oxygen in the air of the drying tubes had been so far replaced by nitrogen as to remove all risk of subsequent explosion.

Meanwhile the globe and condensing tubes were made ready, and first the globe and next the condensing tubes were placed in position, all the rubber connectors required having been previously dried in the current of dry air, and the joints were so contrived that subsequently the stream of gas came in contact with the smallest possible surface of the rubber connectors. The combustion lasted, as has been already stated, from seven to eight hours, and during this time quite a rapid current of air was drawn through the apparatus.

Our preliminary experiments plainly showed that the rapidity of the current within practicable limits had no appreciable effect on our results, and this is due to the fact that the current entered the globe and left the condensers under precisely the same conditions. More than nine tenths of the water was condensed during the first half-hour, the drops falling regularly from the mouth of the inlet tube, and after two hours all traces of cloudiness disappeared from this tube or its connections, showing that the air coming over was perfectly dry. The water thus collected was absolutely clear and limpid.

After the first hour the combustion furnace used for removing oxygen from the air, at the extreme left, was taken away, and by the end of the combustion the reduced copper in the combustion tube proper was again completely oxidized, leaving the globe and all the tubes filled with normal air, as at the beginning of the process. It only remained now to remove the condensers, and reweigh them with all necessary precautions. At both weighings the barometer and thermometer were observed, and the small, usually insignificant correction for buoyancy caused by a change in the atmosphere during the interval was carefully estimated.

The question of the time of running the combustion after the production of water had sensibly ceased was one that was carefully considered. The time mentioned above — eight hours — was far outside the necessary limits, and was reached only after a large number of experiments. That a very long continuance of the current after the combustion was practically ended was unnecessary, was clearly shown by several circumstances. In the first place, the duration of the com-

bustion beyond the limit we have named made no difference in our results, as was repeatedly shown. Again, in one instance, after detaching the condensation tubes and weighing them, they were again put in place and the combustion continued three hours longer, during which time the tubes gained no appreciable weight. In another instance, when a suspicion arose that possibly some hydrogen might be occluded on the walls of the globe, the condensation tubes having been dismounted and weighed as before, the globe was also dismounted and heated over the free flame of a Bunsen lamp to as high a temperature as the glass would safely bear, over 300° C., and then, the apparatus having been remounted, the combustion was continued for one hour. Here again the condensation tubes gained only a small fraction of a milligram in weight, an effect which might easily be accidental, and which was wholly without influence on the result.

#### APPARATUS FOR PREPARING HYDROGEN.

In the preliminary determinations, the hydrogen was drawn from a large copper generator charged with zinc and dilute sulphuric acid. The zinc and sulphuric acid were wholly free from arsenic, and of the best quality, but not absolutely pure; and the writer depended upon an elaborate system of washers and driers for purifying and drying the gas. He found the greatest difficulty in removing the last traces of sulphurous oxide, which hydrogen prepared in this way always car-The presence of this trace cannot be detected by litmus paper, but is immediately indicated by the production of hydric sulphide when the gas is passed over heated platinum sponge; and by interposing a tube containing platinum sponge maintained at a low red heat, followed by a set of potash bulbs, this impurity can be entirely removed. It can also be removed by washing with a strong solution of potassic hydrate alone, if the gas remains long enough in contact with the solu-It was found, however, that a series of potash bulbs was insufficient for this purpose; but two of the long washers represented in the background of Fig. 5 and in Figs. 7 and 8 (Plate), where the gas in small bubbles travels up a tube 51 feet long, are sufficient to remove the sulphurous oxide from even a quite rapid current of hydrogen gas. A series of preliminary determinations was made with hydrogen gas thus prepared and purified, and it was obvious from an inspection of the results, as well as from the difficulties which were experienced in keeping all the joints of this complicated apparatus tight, that the irregularities arose from the diffusion of the air into the hydrogen at some one or other of these joints. It was therefore next sought to

simplify the apparatus, and to depend upon the purity of materials rather than on the completeness of purifying methods for obtaining pure hydrogen. Meanwhile, for reasons stated below, the writer had reduced very materially the scale of his operations, and this rendered unnecessary the large generator we had first employed.

The second apparatus that was constructed is represented in Fig. 5. Of this, the generator, in which hydrogen is made from pure zinc and hydrochloric acid, is the same as that described by Julius Thomsen.\* The Wolff bottle is filled with pure granulated zinc, and the upper bottle contains pure hydrochloric acid diluted about one half. By means of a glass stopcock the acid is allowed to flow into the zinc drop by drop, and in this way the current of hydrogen can be quite

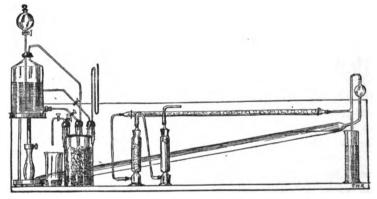


Fig. 5.

closely regulated. Tubes protected by stopcocks are provided for adding fresh charges of acid, and for drawing off the solution of zinc chloride; also a tube connecting the upper part of the two bottles enables the operator to effect these transfers without introducing any air. The gas from this generator passed first through a long potash tube inclined at about 10° to the horizon, then through a tube about three feet long filled with calcic chloride, then through a glass tower filled with glass beads drenched with sulphuric acid, and lastly through a second tower filled with phosphoric pentoxide. As many of the joints as possible were made by fusing together the glass, and all the others were protected by a cement consisting of equal parts of pitch and gutta-percha. It will be noticed that an overflow is provided at the point where the potash tube connects with the calcic chloride tube,

<sup>\*</sup> Thermochem. Untersuch., vol. i, p. 28.

the open mouth of the overflow tube dipping about six or eight inches deep under concentrated sulphuric acid. This overflow indicated the least change of tension of the hydrogen in the apparatus, and would have shown the least leak if it had existed; but the apparatus as thus constructed remained absolutely tight so long as it was in use.

With the hydrogen drawn from this apparatus, the first determinations were not wholly satisfactory, and the cause of error was traced to the air dissolved in the dilute hydrochloric acid with which the generator was charged. In all the succeeding determinations the greatest pains was taken to remove the last traces of air by boiling the dilute acid, and allowing it to cool in a stream of hydrogen; and as additional precaution, while the solution was still warm, the gas was exhausted from the containing vessel and pure hydrogen run in, several times in succession, the pure acid being finally conveyed into the generator entirely out of contact with the air. The need of all these precautions will be seen when it is considered how small an admixture of air or of nitrogen will materially influence the weight of the hydrogen. If only one ten-thousandth of the volume of the hydrogen were replaced by air during the process of filling the globe, this would cause an apparent increase of weight in the hydrogen of five tenths of a milligram, and that, other things being equal, would reduce the atomic weight of oxygen two hundredths of a unit.

The precautions used in filling the globe have already been described in detail, and with hydrogen from the apparatus, constructed and charged as just described, were made the five consecutive determinations whose results are given as of the first series in the table on page 173. These, and all the determinations given in the table, were made by the writer's pupil and assistant, Mr. Theodore William Richards, to whose experimental skill the success of the investigation is largely due, and without whose assistance the work could not have been completed in the present condition of the writer's sight. The mean of these first five results, as will be noticed, is but little less than that obtained by Dumas, and the probable error,  $\pm 0.0048$ , is considerably less than that of Dumas. In order to understand how this result appeared to the writer, it must be remembered that he started with a certain prepossession in favor of the hypothesis of Prout, based on his previous work on antimony; and, furthermore, that the effect of the · causes of error which had been encountered and overcome all tended to lower the atomic weight; and the result obtained was a maximum which had been reached after every known precaution had been taken. But although this maximum was essentially the same as that obtained

by Dumas by an obviously less direct and less accurate method, yet it was still possible that there might be some constant error, and that some cause might yet be found which would raise the maximum by the forty-six thousandths required to give the whole number 16. was true that the probable error was only about one tenth of this difference: still, as the materials had been purified, the maximum had constantly risen, and the theoretical limit was in sight. In reviewing the work, it was obvious that the degree of accuracy of the methods used for determining the weights both of the hydrogen and of the water was so great, that no possible error in these values could account for the difference in question. This would imply an error of 1.2 milligrams in the weight of the hydrogen, and of 10.8 milligrams in the weight of the water, and the possible error of a single determination leaving out of account the reduced probable error of the average value - was far within these limits. If there was a constant error, it must result from the want of purity of the hydrogen gas, and we therefore determined to try another method for preparing the hydrogen.

The apparatus next used is represented in Fig. 7 (Plate), and differs from the last only in the generator. Here the generator is a threenecked bottle having a capacity of about two litres, filled to about one eighth of its capacity with a semifluid amalgam of mercury and pure zinc. On this rests dilute hydrochloric acid, containing about twenty per cent of HCl, nearly filling the bottle. Into this acid dips a platinum electrode, while a straight glass tube passing through the middle neck and dipping under the amalgam gives the means of establishing an electrical connection between the large platinum plate which forms the negative electrode and the amalgam. In addition, a siphon tube for drawing off the acid when saturated with zinc, a funnel tube for introducing a fresh charge, and an exit tube, all well cemented to the several necks of the bottle, complete the generator. When the electrical connection is broken, all chemical action ceases, but on connecting by a wire the platinum electrode with the amalgam, a very steady but slow evolution of hydrogen gas takes place, which can be regulated with the greatest nicety by varying the resistance of the connecting wire. On interposing two cells of a Bunsen battery the evolution of gas becomes very rapid. Besides its special use in this connection, the apparatus will be found of great value as giving an absolutely constant source of pure hydrogen whenever required. In charging the generator with acid, the same care was taken to exclude every trace of air as with the previous apparatus, and with hydrogen thus prepared a second series of five consecutive determinations was made, whose

results are given in the table on page 173, below those of the first series; and it will be noticed that, while the average value obtained is essentially identical with the previous result, the agreement of the several determinations is more close, and in consequence the probable error is reduced more than one half. A closer agreement under the circumstances could not possibly be expected.

Such a striking confirmation of the previous result seemed very conclusive, and the very small probable error indicated a command of the method which was very satisfactory. Still, it could not be proved that there might not be a constant impurity in the hydrogen used. As the hydrogen had passed every possible chemical test unimpeached, the only possible impurity that could be suspected was nitrogen, and Mr. Richards therefore made a careful spectroscopic examination, searching for the more conspicuous nitrogen lines in the spectrum obtained by passing an induction current through a rarefied atmosphere of the gas from the generator just described; but not the faintest trace of any of these lines could be seen.

Still, as in the electrolytic method of preparing the hydrogen the same materials, hydrochloric acid and zinc, were used as in the first series of experiments, it was determined to procure hydrogen by a wholly different chemical process, using the well-known reaction of metallic aluminum upon a solution of potassic hydrate.

The purest aluminum sheet that could be obtained in the American market was procured for the purpose, and the apparatus represented in Fig. 8 (Plate) was used for generating the gas. The generator here was a simple flask holding a strong solution of chemically pure potassic hydrate, and the aluminum was introduced in small pieces through a large open tube, - dipping under the surface of the solution, - the liquid being maintained at a level near the open mouth of the tube by the tension in the interior of the apparatus. The small strips of aluminum were carefully cleaned, and caused slowly to slide down the tube; the evolution of hydrogen from the surface began as soon as the strips of metal touched the liquid, and became very active in the tube before they dropped into the flask. And this action insured the removal of any traces of air which might adhere to the surface. this apparatus the long caustic potash washer was not used, as being no longer necessary, and the gas was passed through caustic potash bulbs to remove the spray, and then through a calcic chloride tube, and over sulphuric acid and phosphoric pentoxide, as before.

With hydrogen thus prepared, the six determinations of the third series in the table were made; and it will be seen that the average of

the results is a value which is essentially identical with the average values from the other two series. The probable error in this last series is larger than in the second, although still very small; but the difference is due, as the note-books plainly show, to the different conditions under which the two series were made. As before stated, the compensation of the balance was perfect, and the apparent weight of the globe did not alter by a tenth of a milligram, even with wide variations of temperature and pressure, so soon as those changes became constant. But when the changes of temperature in the balanceroom were rapid, currents of air were established in the case, however great care was taken in protecting it, which rendered the apparent weight irregular to the extent of one or two tenths of a milligram; and the third series was made under less favorable conditions in this respect than the second. This point is illustrated by the following notes of two determinations, which are given in full, in order that all the circumstances connected with the determinations may be seen.

# SERIES II. Determination 5.

```
Weighings of the globe: -
                                                       Grams.
  Exhausted.
                         June 6th, 6.00 \text{ p. m. Tare} = 0.1960
                               7th, 7.25 A. M.
                                                    = 0.2011
                                    8.30 A. M.
                                                    = 0.2011
                           46
                                   11.20 A. M.
                                                    = 0.2011
                                    2.00 P. M.
                                                 46
                                                    = 0.2011
                                                       0.2011
  Filled with Hydrogen. June 7th, 7.20 p. m. Tare = 0.6100
                                                    = 0.6156
                               8th, 8.00 A. M.
                           "
                                " 10.00 а. м.
                                                    = 0.6156
                                " 12.15 р. м.
                                                = 0.6154
                                    7.50 A. M.
                                                 " = 0.6155
                           4
                                    9.30 A. M.
                                                    = 0.6155
                                " 11.40 а. м.
                                                 = 0.6155
                                                      0.6155
```

Weight of Hydrogen taken = 0.6155 - 0.2011 = 0.4144 gram. The combustion was started at 11 A. M., and stopped at 6 P. M.

Weight of P2O5 tube,

before combustion	$\mathbf{a} = 48.2499$	h = 29.58	t = 26.0
after "	=48.2529	h=29.76	t = 23.5
Gain in weig	ht = 0.0030	+ 0.18	<b>— 2.5</b>

Weight of H<sub>4</sub>SO<sub>4</sub> tube,

before combustion = 62.3959 
$$h = 29.58$$
  $t = 26.5$ 
after " = 66.1076  $h = 29.75$   $t = 23.5$ 
Gain in weight = 3.7117  $+ 0.17$   $- 3.0$ 

The correction to vacuum for 3.7117 grams of water weighed with brass and platinum weights is 4.1 mg.

Gain in weight of 
$$H_3SO_4$$
 = 3.7117 grams.

" "  $P_3O_5$  = 0.0030 "

Correction to vacuum = 0.0041 "

for  $t$  and  $h$ ,  $P_3O_5$  = 0.0004 "

" " "  $H_2SO_4$  = 0.0005 "

Total  $H_3O$  formed = 3.7197 "

Weight H taken = 0.4144 "

Weight O combined = 3.3053 "

Atomic weight of Oxygen = 
$$\frac{2 \times 3.3058}{0.4144}$$
 = 15.953

% H in water = 11.140.

% O in water = 88.860.

#### SERIES III. Determination 5.

Weighings of the globe: -Grams. Exhausted. 8th, 7.45 A. M. Tare = 0.1127Nov. = 0.112511.10 A. M. " 12.00 м. = 0.11225.00 р. м. = 0.1122" 9th, 8.40 a. m. " = 0.1121" 9.15 а. м. = 0.1119" 12.40 p. m. " = 0.1120" " 4.00 p. m. " = 0.112110th, 8.40 A. M. " = 0.1119" 10.40 A. M." = 0.112011th, 8.40 A. M. " = 0.1121" 10.15 a. m. " = 0.1120Average " = 0.1120

Grams. Filled with Hydrogen. Nov. 11th, 12.45 p. m. Tare = 0.532566 4.00 P. M. = 0.5348" = 0.53286.00 P. M. 12th, 12.00 m. = 0.527314th, 8.00 A. M. " = 0.52739.30 а. м. 66 = 0.527311.15 а. м. " = 0.5273Tare filled with H = 0.5273" empty = 0.1120Weight H = 0.4153

The combustion was started at 11.25 A. M., and stopped at 6 P. M.

# Weight of P2O5 tube,

before combustion = 
$$48.1795$$
  $h = 30.03$   $t = 16.5$  after " =  $48.1832$   $h = 30.00$   $t = 18.0$  Gain in weight =  $0.0037$   $-0.03$   $+1.5$ 

# Weight of H<sub>2</sub>SO<sub>4</sub> tube,

before combustion = 
$$64.9625$$
  $h = 30.03$   $t = 16.5$  after " =  $67.6832$   $h = 30.00$   $t = 18.0$  Gain in weight =  $3.7207$   $-0.03$   $+1.5$ 

Gain in weight of 
$$H_2SO_4$$
 = 3.7207 grams.  
" "  $P_2O_5$  = 0.0037 "

Correction to vacuum = 0.0041 "

3.7285 "

Correction for 
$$t$$
 and  $h$ ,  $H_2SO_4 = -0.0002$  "  
"  $P_2O_5 = -0.0002$  "

Total 
$$H_2O$$
 formed = 3.7281 "
Weight H taken = 0.4153 "
Weight O combined = 3.3128 "

Atomic weight of Oxygen = 
$$\frac{2 \times 3.3128}{0.4153}$$
 = 15.954

$$\%$$
 H = 11.139.  $\%$  O = 88.861.

## ATOMIC WEIGHT OF OXYGEN.

# Table of Final Results.

## SERIES I.

Weight of Hydrogen.	Weight of Water.	Atomic Weight of Oxygen.
0.4233	3.8048	15.977
0.4136	3.7094	15.937
0.4213	3.7834	15.960
0.4163	3.7345	15.941
0.4131	3.7085	15.954

Average =  $15.954 \pm 0.0048$ 

# SERIES II.

0.4112	<b>3.693</b> 0	15.962
0.4089	3.6709	15.955
0.4261	3.8253	15.955
0.4197	8.7651	15.942
0.4144	3.7197	15.953

Average =  $15.953 \pm 0.0022$ 

## SERIES III.

	Average	$=15.952 \pm 0.0035$
0.4167	3.7435	15.967
0,4153	3.7281	15.954
0.43205	3.8748	15.937
0.4205	3.7776	15.967
0.4284	3.8436	15.944
0.42205	3.7865	15.943

Total average =  $15.953 \pm 0.0017$ 

Dumas's value =  $15.960 \pm 0.0070$ 

On examining the table, it will be noticed that the mean of the determination by the electrolytic method is the mean of all the determinations combined, and that the probable error of the total average is only about one fourth as great as the error of the nineteen determinations of Dumas, which are incomparably the best that have hitherto been made.

It does not now seem possible to escape from the conclusion, that the proportions in which the purest hydrogen that can be made combines with oxygen to form water are those of 2 to 15.953, with a possible error far within the  $\frac{1}{100}$  of a single unit.

The question, of course, still remains, Is the hydrogen thus prepared the typical hydrogen element? But this is the same question which must arise in regard to any one of the elementary substances; and all that we can say is, that the evidence in regard to the purity of the hydrogen we have used is as good as any that can be adduced in regard to any one of the elementary substances whose atomic weight has been most accurately determined. The question as regards Prout's hypothesis narrows itself now to this one point; and here we must be content to leave it until further investigation has given us more knowledge in regard to the nature of elementary substances.

The writer at first planned to carry out the investigation on a much larger scale, and for the purpose had blown a globe similar to that represented by Fig. 1, but of five times the capacity, and counterpoised it by the same general method. This globe held twenty-five litres (somewhat over two grams of hydrogen gas), or five times as much as the globe actually used; but the difficulties of carrying out the determinations on this scale led him to reduce the scale of the determinations to that actually adopted; and in the view of the results finally reached, it is evident that no appreciable advantage would have been gained from the enormous expenditure of time and labor which the process on a large scale involves. Assuming that the difficulties of preparing pure hydrogen gas on that scale could have been overcome, it would have required from five to seven hours to fill the globe, and four or five days continuously to complete the combustion.

Moreover, after many trials, the writer could not procure a globe that would stand the requisite pressure weighing less than two and one half kilograms, and with this weight and volume it was not possible, with the best balance he could command, to distinguish half a milligram with as much accuracy as he could one tenth of a milligram with the smaller apparatus, while a vastly longer time was required to reach equilibrium. A great deal of time was spent in

endeavoring to perfect this larger apparatus, and a very thorough knowledge was acquired of its relative efficiency. The greatest gain that could have been expected in carrying out the work on this scale would have been the reduction of the probable error to about one half of the present amount, but it is obvious that this gain could be of no importance in the present condition of the science. The accuracy we have reached is far beyond the demands of any analytical work; and, as we have shown, the theoretical question in regard to Pront's law has been settled so far as analytical work can solve the problem. It now turns solely on the typical character of the material we call hydrogen, when prepared in the purest condition known to modern science.

In considering the bearing of the result now published on Prout's hypothesis, it must be borne in mind that it confirms in a most striking manner the result of Dumas, based on the weight of oxygen which water contains, and in connection with his results furnishes a complete analysis of water, with a degree of accuracy as great as can be expected, or as has ever been obtained, in any analytical work.

## Complete Analysis of Water.

It must be remembered that in Dumas's investigation the oxygen alone was weighed, while in the present investigation the hydrogen alone was weighed, and the fact that these two wholly independent analytical results made under such widely different circumstances exactly supplement each other within the limits of probable error, is an evidence of accuracy and a proof of finality which is irresistible.

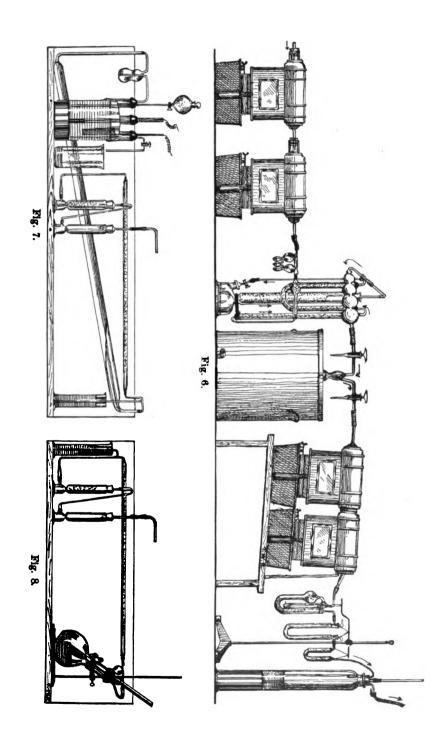
It would have been highly desirable, if it had been possible, to determine both the oxygen and the hydrogen in one and the same analytical process, as the writer succeeded in doing in the case of silver, bromine, and antimony, and he made many experiments on the reduction of oxide of silver by hydrogen with this view. He succeeded in preparing pure oxide of silver, of definite composition, but the investigation was interrupted by the failure of his sight before he was able to overcome the grave experimental difficulties which he process presented. In view, however, of the present results, it is doubtful whether any advantage would have been gained by that mode of

experimenting, for no more certain confirmation could have been reached than that furnished by a comparison of Dumas's results with those of this paper.

Since this investigation was essentially finished, and the results communicated to the American Academy at their meeting of June 15, 1887, we have received from the author a "Sonderabdruck" from the "Berichte der Deutschen Chemischen Gesellschaft," dated the 26th of July following, and entitled: "E. H. Keiser: Ueber die Verbrennung abgewogener Mengen von Wasserstoff und über das Atomgewicht des Sauerstoffs." In this paper Mr. Keiser distinctly recognizes the importance of directly weighing the hydrogen in the determination of the atomic weight of oxygen, and quotes the remarks of Dumas given above. He has also devised a very ingenious method of weighing hydrogen when occluded by palladium; but the preliminary results he publishes are far from having the degree of accuracy required, and lead us to infer that, like our own preliminary results, they must be vitiated by varying impurities in the hydrogen gas used. The three determinations whose results he publishes gave for the atomic weight of oxygen respectively 15.873, 15.897, and 15.826.

We are sorry if Mr. Keiser has entered on somewhat the same field which we have so long occupied without knowledge of our work. But, as above stated, our investigation was begun more than five years ago; and the methods employed have been freely explained to the many chemists, both American and European, who have visited Cambridge during the interval. We earnestly hope that Mr. Keiser will carry out his investigation; for so important a constant as the atomic weight of oxygen cannot be too often verified.

J. P. C. CAMBRIDGE, December 15, 1887.



#### XI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE. — J. P. Cooke, Director.

# FURTHER INVESTIGATION ON THE ATOMIC WEIGHT OF COPPER.

By Theodore William Richards.

Presented by J. P. Cooke, June 15, 1887.

In the last volume of these Proceedings there appeared a description of a new determination of the atomic weight of copper, based upon the precipitation of silver from a neutral solution of argentic nitrate by pure metallic copper. In the course of some further experiments, it became necessary to ignite a portion of the silver from determination No. 5 of that series; and it was found that two grams of silver lost four tenths of a milligram by this process. It is thus evident that 150° is not a temperature high enough to drive out all the water from the silver, and hence the results before given are incorrect by a slight amount. In this determination the weight of the silver was 3.39035 grams, after drying at 150°, hence its weight after ignition would have been 3.38975 grams. The weight of copper taken was .9987 grams, therefore the corrected atomic weight of copper would be 63.452, instead of 63.437.

Unfortunately, all the silver formed in the other determinations had been employed in testing for the presence of copper; hence it was impossible to determine whether the other samples would lose water on heating in a similar manner. It seemed, therefore, desirable to make a new series, using samples of pure copper, prepared from the ores of different localities. Should the result be the same in each instance, we should have a very strong proof, not only that the copper used in each case was pure, — because the different samples would probably contain different impurities, — but also that the atomic weight of copper is a perfectly constant quantity.

The method used was exactly that of the previous paper, although more difficulty was found in keeping the solution below zero for VOL. XXIII. (N. S. XV.)

twenty-four hours than was the case before, because of the warmer weather. Several determinations had to be rejected because the temperature rose above zero, and copper was precipitated with the silver. Upon splitting open the fine crystalline plates of silver precipitated in these rejected experiments, a light green precipitate of basic cupric nitrate was found adhering to the inner surface, which could not be removed by continued washing with cold water. The presence of this precipitate explains the admixture of copper with the silver precipitated above zero, and points at once to the mechanism of the chemical action.

When copper is placed in a solution of argentic nitrate, two reactions take place, and the temperature regulates the predominance of one or the other. The chief reaction is the simple one ordinarily written; it alone is active between 0° and -5°, and it is the chief one even at 100°. The secondary reaction, which is active at 100°, but which entirely ceases below 0°, may perhaps be written thus, — assuming that the basic nitrate has the formula usually assigned to it:—

$$\begin{array}{c} 4 \, \text{AgNO}_{\$} + 4 \, \text{Cu} + 3 \, \text{H}_{2}\text{O} = \\ \text{Cu(NO}_{\$})_{\$} \, . \, \, 3 \, \text{Cu(OH)}_{\$} + 2 \, \text{Ag}_{\$} + \text{NO} + \text{NO}_{\$} \end{array}$$

Evidently in this reaction the copper precipitates only one half of its equivalent of silver. It will be remembered that an evolution of nitrous fumes was previously observed, when the temperature rose above the freezing point.

The argentic nitrate used in the new series was prepared as before, except that even greater precautions were taken to insure its purity, by successive crystallizations and fusions.

Two samples of copper were used, one from Lake Superior, the other from Germany. For the purification of the former, the sample was dissolved in sulphuric acid, with the addition of nitric acid; the solution was evaporated to dryness, and the solid heated over asbestos in a porcelain dish, until the fumes of sulphuric acid ceased coming off. The cupric sulphate was now dissolved in water, crystallized twice, and the diluted solution of the last crystals boiled and shaken with a little potassic hydrate for three hours. The solution was now filtered, and the cupric sulphate was crystallized several times from hot water. Finally, the solution of the last pure crystals, strongly acidified by sulphuric and a little nitric acid, was decomposed by the current of a Bunsen cell, and the chemically pure copper deposited on thick platinum foil.

The second example of copper was prepared from German cupric

oxide in a similar manner, except that the sulphate was crystallized a greater number of times. In this connection it may be mentioned that, of many samples of German cupric oxide tested, not one was found which did not contain a comparatively large amount of arsenic. In the case of many samples, after several reductions with pure hydrogen and oxidations, the arsenic will actually sublime off as arsenious oxide; and a quantity of the substance was collected in this manner.

The method of cleaning the copper was similar to that previously adopted; it was treated in succession with dilute potassic hydrate, dilute sulphuric acid, and a very large amount of water, and then dried and reduced by pure hydrogen.

The silver which was obtained by precipitation from the pure argentic nitrate was first washed and dried at 150°, and weighed, as before; and was then heated to incipient redness, and weighed again. The loss of weight by this process varied with the different samples between three tenths of a milligram and one milligram. The Gooch crucible and asbestos mat subjected to the same treatment did not lose an appreciable quantity. The results were calculated for the weight of silver both before and after ignition, and it will be noticed that the first column of results corresponds almost exactly to the results given in the previous paper. The silver was in each case tested for copper, and no trace was found.

RESULTS.
GERMAN COPPER.

No. of	Weight of Silver formed.			Atomic Weight Ou (Ag = 107.675).		
Experi- ment.	Weight Cu.	Before Ignition.	After Ignition.	Cu : Ag <sub>2</sub> == 1 : n.	Before Ignition.	After Ignition.
1	Grams. 0.75760	Grama. 2.5723	Grams. 2.5718	8.3940	68.426	68,450
2	0.95040	8.2261	8.2256	8.8939	68.440	68. <del>4</del> 51
3	0.75998	2.5798	2.5794	8.8942	63.438	63.447
	······		<u> </u>	··	Average	68.449

Greatest variation =  $\pm .002$ . Probable error =  $\pm .0010$ .

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No. of	Weight Ag formed.			Atomic Weight Cu (Ag = 107.675).		
Experi- ment.	Weight Cu.	Before Ignition.	After Ignition.	Cu : Ag <sub>2</sub> = 1 : n.	Before Ignition.	After Ignition.
	Grame.	Grams.	Grame.			
4	1.02060	8.4650	3.4640	8.3942	63.482	63.448
5	0.90460	8.0705	3.0701	3.8989	68.444	68.452
	ا		<u></u>	<u>'                                    </u>	Average	, 68.450

LAKE SUPERIOR COPPER.

The average of these two series is 63.450, with greatest variations of  $\pm .002$  and  $\pm .003$ , and a probable error of  $\pm .0006$ . The average of the results calculated from the weight of silver dried at  $150^{\circ}$  is 63.436, while the results published in the preceding paper gave 63.437.

The complete concordance of these results with each other, and with the previous value above referred to, would point strongly to the following conclusions.

First, that the copper used in each case was absolutely free from metallic alloy; for manifestly the three entirely different samples would be likely to contain different impurities, or at least different amounts of the same impurity. The copper was tested for sulphur with the greatest care by solution in nitric acid and treatment with baric chloride, and no trace of cloudiness was perceptible. That the copper was absolutely free from impurity is not contended; only that it did not contain a weighable amount of impurity in one gram, the amount used in each experiment. It is manifest that attempts to purify the copper beyond this limit would be labor thrown away, and would produce no effect upon the atomic weight. For example, one tenth of a milligram is a very large amount of foreign material to suppose existing in a gram of copper purified with such care; but this large amount would only change the atomic weight five units in the third decimal place, - a quantity which is of no consequence when the atomic weight is in doubt three units in the first decimal place.

Another and still more positive conclusion reached by these results is that the atomic weight of copper is a constant quantity with reference to nitric acid and silver. If copper had a variable atomic weight, it would surely appear in specimens taken from such widely different

sources. This conclusion still remains in force, even supposing there be a constant error in the process, for the constant error must affect all the results equally, and could not possibly equalize unlike results.

A third conclusion pointed out by the determinations is that the argentic nitrate was the normal compound, and quite pure; for it will be remembered that two entirely different samples had been used in the course of the work.

There is but one point which remains to be considered, and that is the existence or non-existence of a constant error in the reaction. That this is by far the most important point in the whole discussion, it is unnecessary to state. Whether there be such a constant error, future investigations may show; for the present, it is sufficient to say that it is extremely difficult to see where such an error might creep in. The whole reaction is so simple and so sharp, that the probability of error is reduced to a minimum, and in every case any possible cause of error has been guarded against.

Professor Cooke, under whose direction the whole investigation has been conducted, suggested that similar experiments be made, using argentic sulphate instead of the nitrate; but after a large number of trials this was found to be impracticable: first, because the solution has a much higher freezing point than that of the nitrate; and secondly, because the solution was necessarily so dilute, on account of the slight solubility of argentic sulphate, that the complete precipitation of the silver required a much longer time, giving more opportunity for secondary reactions. The silver was always accompanied by a very slight admixture of some basic cupric sulphate; and hence this method, which, if successful, would have been able to throw much light on the question of a constant error in the previous results, had to be abandoned.

CAMBRIDGE, December 15, 1887.

#### XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE. — J. P. COOKE, Director.

## ADDITIONAL NOTE ON THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.

By Josiah Parsons Cooke and Theodore William Richards.

#### Presented March 14, 1888.

THE preceding paper on this subject was already in print, and a number of the extra copies had been distributed, when the writer received a letter from Lord Rayleigh stating that he had been engaged on a similar work, and had observed that the glass balloon used in Regnault's method of weighing gas volumes, when exhausted, was sensibly condensed by the pressure of the air. Obviously, if this were true, the tare of the balloon thus exhausted would be too large in consequence of the lessened buoyancy of the atmosphere, and hence the subsequently observed weight of gas when the balloon was filled would be too small. A shrinkage amounting to a single cubic centimeter would make a difference of about 1.29 milligrams, and Lord Rayleigh suggested that our results might have been influenced by a constant error arising from this source. As the same balloon represented in Figure 1 of the preceding paper had been used in all our determinations, and was still in good condition, there was no difficulty in determining the amount of shrinkage under exhaustion, and thus finding the correction which ought to be applied to the results on this account. The method we used was briefly as follows.

The balloon was first exhausted, and then completely filled with boiled distilled water at an observed temperature. The weight of this water having been taken, and the internal volume of the balloon thus determined, a small portion of the water—190 cubic centimeters—was run out, and the volume estimated both by direct measurement and also by reweighing the balloon. With these data we could readily calculate the volume of air left in the balloon for any given temperature, and the small amount of water lost by evaporation in the

subsequent exhaustion produced no sensible effect on the result, as a knowledge of the volume within five cubic centimeters was all that the present problem required, and the water did not lose in weight more than two grams during the whole series of experiments.

The balloon was now thoroughly exhausted, allowed to stand, and again exhausted several times, until a vacuum gauge connected with it remained constant over night, and indicated the calculated tension of aqueous vapor, which showed that all the air — dissolved or otherwise — had been practically removed.

A sufficient mass of water was left in the balloon to sink it under water, and thus immersed in a large vessel filled with distilled water, (which had been boiled and allowed to cool,) it was now suspended from the beam of the balance used throughout this investigation. air bubbles formed on the glass, and care was taken to remove all entangled air from the connecting tubes. The weight soon became constant, and the tare could be accurately determined within a centigram. The connecting tubes of the balloon were next lifted above the surface of the water, and, after carefully drying the inlet, the outside air was admitted, and the temperature of the water in the tank and the height of the barometer observed. On again immersing the balloon there was a large loss of weight, - about 1.4 grams, - over six times the weight of air admitted, - only about 0.2 gram. There had evidently been a marked shrinkage under exhaustion amounting to about 1.6 cubic centimeters. This decrease of weight was noted after the equilibrium had become constant, usually in about five minutes.

It is probable that the admitted air was saturated with moisture, and the calculation is based upon that assumption; but this would make no practical difference in the weight so far as the problem before us is concerned. Appended is an example of the method.

# SERIES I. Determination 2.

Tare of globe exhausted = 198.22 grm. 
$$T^{\circ} = 17^{\circ}.30$$
.

"filled =  $196.83$  "  $T^{\circ} = 17^{\circ}.30$ .

Observed loss of weight =  $1.39$  "

Atmospheric pressure = 
$$75.86$$
 c. m.  
Tension of aqueous vapor =  $1.46$  "

Difference =  $74.40$  "

Weight of 188 c. c. moist air at 17°.3 and 74.4 cm. = .22 grm. Observed loss of weight of globe = 1.39 "

Water displaced by difference of volume = 1.61 "

Diff. of volume corresponding to 74.4 cm. pressure = 1.61 c. c.

" " 76.8 cm.\* " = 1.66 c. c.

Weight of 1.66 c. c. of air at 76 cm. and 22° C.\* = 1.98 mg.

Below are given the data of the two series of determinations which were made.

SERIES I.

Number.	Loss of Weight. Grams.	Atmospheric Pressure. Centimeters.	Temperature.	Correction. Milligrams.
1.	1.34	76.40	18.10	1.92
2.	1.39	<b>75.86</b>	17.30	1.98
3.	1.89	75.80	17.32	1.98
4.	1.37	<b>7</b> 5.78	17.40	1.96
5.	1.39	75.75	17.45	1.99
				1.97
		Series II.		
6.	1.38	<b>75</b> .60	14.50	1.98
7.	1.39	<b>75.60</b>	14.50	2.00
8.	1.39	75.58	14.60	1.99
9.	1.40	75.58	14.61	2.01
10.	1.39	75.58	14.65	1.99
				1.99

Total average, 1.98 milligrams.

The quantity 1.98 milligrams is then the correction sought, and this closely agrees with Lord Rayleigh's estimate of the value in the letter above referred to. Since in the work described in the preceding paper all the data required for the calculation were not recorded in every case, it will be impossible to apply this correction to each determination separately. But no sensible error can result if we add the correction to the average apparent weight of the hydrogen, easily calculated from the data given in the table on page 173.

<sup>• 22°</sup>C. and 76 cm. pressure were the average atmospheric conditions at the times of weighing the globe in the previous determinations, and 76.8 cm. was the average difference of the pressure on the globe when exhausted and full of hydrogen.

The total weight of the hydrogen burnt in the sixteen determinations as observed was 6.7029 grams. Add to this sixteen times the correction, or  $16 \times 0.00198 = 0.0317$ , and we obtain 6.7346 grams for the corrected weight. The total weight of the water formed was 60.1687 grams. Hence we find by difference for the total weight of oxygen consumed in the combustions 53.4341 grams; and the corrected atomic weight of oxygen is  $2(53.4341 \div 6.7346) = 15.869$ .

The probable error of this result is no greater than that of the "Total average" given on page 173; for the value of the constant correction must be certainly known within the one fiftieth of a milligram. It is true that there are several variable elements which enter into the determination of this value, but they can all be estimated with far greater accuracy than the conditions of our problem require. We may therefore write as the present result of our work, H:O=1.000:15.869.

## Atomic weight of oxygen, 15.869 $\pm$ 0.0017.

If we compare this result with that of Dumas, as before, on page 175, we have for the complete analysis of water,—

Percentage of oxygen after Dumas . . . 88.864  $\pm$  0.0044 Percentage of hydrogen after final result .  $\frac{11.198 \pm 0.0011}{100.057}$ 

It would now appear that the close agreement before shown was a mere coincidence, and that there must have been a small constant error either in our own process or in that of Dumas. Where the error lies further investigation can alone determine; for although, after a careful revision of our work, we can discover no flaw, no one can be confident that such a constant error as has already appeared may not hereafter be found, - and certainty can only be secured after repeated confirmations by essentially different methods. While, therefore, we feel bound to acknowledge without delay the cause of constant error which Lord Rayleigh has pointed out, we give our corrected result as subject to further revision. It has been suggested by Lord Rayleigh, in a " Preliminary Notice" of his work on the relative densities of hydrogen and oxygen, of which advance sheets have been received while writing this note, that in our combustions the hydrogen may have been imperfectly burnt, especially as towards the last of the combustion it must have been greatly diluted (but with air). We have no decisive evidence on this point; but the whole course of our combustions assured us that this could not be the case. During the first stage of the combustion, when pure hydrogen was passing into the combustion tube, and while water was dropping into the condenser (Figure 4, page 163), there would often be several minutes—during which the larger part of the water was condensed—when no residual gas whatever would be seen to escape, and the bubbling of the gas through the sulphuric acid at the bend of the U tube made the least overflow perfectly evident. Again, the oxide of copper in the combustion tube was always reduced to a perfectly definite limit, leaving at least seven eighths of the tube in which the black oxide was apparently wholly unchanged. Further, it is not probable that an error arising from the imperfect combustion of the hydrogen would have a constant value. The unconsumed residue must vary greatly with the conditions of the experiment; and such an agreement as that exhibited by the results on page 173 could never have been obtained under such circumstances.

It seems unnecessary to add, that every precaution was taken in our work which our experience could suggest, and that a great amount of labor was spent on such details which does not appear in the published results. Both the balances and weights employed were most carefully verified. The water formed by the combustion was tested, and the dissolved air taken into account. We mention these points because they have been noticed by correspondents; but many similar details which were worked out and set one side we have not thought it necessary to describe in our paper. In writing such a paper elementary principles must be assumed.

In adopting Regnault's method for weighing the hydrogen used in our determinations, we assumed with him that the glass balloon used in the work remained practically constant, whether exhausted or filled with gas. We never questioned this assumption, not only because we had the greatest confidence in all Regnault's work, but also because we knew that he had himself carefully investigated the behavior of glass bulbs under pressure; and indeed he treats the subject fully in the paper immediately preceeding his classical paper on gas density.\* Moreover, we made with our apparatus a preliminary determination of the density of air, and obtained Regnault's number within the limits of the uncertainty in regard to the value of the force of gravity at this place. Regnault's values for the weight of one litre, not only of air, but also of nitrogen, oxygen, hydrogen, and carbonic dioxide, have



Mémoires de l'Acad. Roy. des Sciences de l'Inst. de France, vol. xxi. pp. 106 and 121.

been hitherto regarded as among the most trustworthy data of science. His determinations were all made by the method of counterpoise which we adopted in our work, and he used balloons of twice the volume of those we employed. When exhausted, the glass must have been condensed to an even greater extent than has been shown above; but no account whatever is taken of this shrinkage. As Regnault's constants have been universally used, it is obvious that Lord Rayleigh's correction must be applied to all determinations of gas or vapor densities hitherto made, and to all atomic weight determinations of any kind which involve the calculation of the weight of a measured volume of any gas or vapor. Except, however, in the case of hydrogen, the correction will be inconsiderable.

J. P. C. CAMBRIDGE, March 15, 1888.

### XIII.

# CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

#### ON SUBSTITUTED PYROMUCIC ACIDS.

SECOND PAPER.

BY HENRY B. HILL AND ARTHUR W. PALMER.

Presented March 14, 1888.

#### ON SULPHOPYROMUCIC ACIDS.\*

Pyromucic acid shows in many of its reactions so close an analogy to benzoic acid that a study of its behavior toward concentrated sulphuric acid could hardly fail to yield interesting results. In 1860 Schwanert † prepared a sulphopyromucic acid by distilling sulphuric anhydride slowly over powdered pyromucic acid. The barium salt was said to be not distinctly crystalline, and its composition was established by a single determination of barium in the salt dried at 150°. With the exception of the brief notice by Schwanert, we have been able to find no mention of furfuran derivatives containing the sulphogroup. We have found that a sulphopyromucic acid is formed without difficulty when pyromucic acid is dissolved in fuming sulphuric acid, and that a second sulphonic acid may readily be made by indirect methods. We have also prepared and studied several derivatives of these sulphonic acids containing bromine, and have succeeded in establishing the constitution of these various products.

#### 8-Sulphopyromucic Acid.

If dry pyromucic acid is slowly added to fuming sulphuric acid (Sp. Gr.1. 95), it dissolves without serious discoloration, and in a short

<sup>\*</sup> A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University in May, 1886, by Arthur W. Palmer, then candidate for the degree of Doctor of Science.

<sup>†</sup> Annalen d. Chem. u. Pharm., cxvi. 268.

time the formation of the sulphonic acid is complete. We have usually taken three parts of sulphuric acid to one of pyromucic, and have allowed the viscous solution to stand for twenty-four hours before diluting and neutralizing with baric carbonate. The aqueous solution filtered from the baric sulphate and concentrated by evaporation deposits on cooling globular aggregations of minute crystals, which are readily purified by recrystallization from hot water. The acid prepared by exact precipitation with sulphuric acid is extremely soluble in water, but may be obtained by concentration in large transparent prisms which deliquesce in moist air.

Baric &-Sulphopyromucate, BaC<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. 4 H<sub>2</sub>O. — This salt crystallizes in thin flat prisms, which are usually closely aggregated in hemispherical masses. It is readily soluble in hot water, more sparingly soluble in cold water, and its aqueous solution is precipitated by the addition of alcohol. When dried by exposure to the air it contains four molecules of water, a part of which it slowly loses over sulphuric acid or at 100°, the rest at 160°.

I. 2.1205 grm. of the air-dried salt lost, at  $162^{\circ}$ , 0.3827 grm.  $H_2O$ . II. 2.5754 grm. of the air-dried salt lost, at  $160^{\circ}$ , 0.4605 grm.  $H_2O$ .

	Calculated for	Found.	
	BaC <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> . 4 H <sub>2</sub> O.	I.	II.
H.O	18.02	18.05	17.88

I. 0.7695 grm. of the salt dried at 160° gave 0.5480 grm. BaSO<sub>4</sub>. II. 0.7010 grm. of the salt dried at 160° gave 0.4990 grm. BaSO<sub>4</sub>.

	Calculated for	Found.		
	BacsH <sub>2</sub> SO <sub>6</sub> .	I.	II.	
Ba	41.90	41.87	41.85	

The solubility of the salt in cold water we have determined according to the method of V. Meyer.

- I. 15.1350 grm. of a solution saturated at 21° gave 0.3672 grm. BaSO<sub>4</sub>.
- II. 13.9856 grm. of a solution saturated at 21° gave 0.3384 grm. BaSO<sub>4</sub>.

The aqueous solution saturated at 21° therefore contained the following percentages of the anhydrous salt:—

Acid Baric & Sulphopyromucate, Ba(C<sub>5</sub>H<sub>3</sub>SO<sub>6</sub>)<sub>2</sub>. 4 H<sub>2</sub>O and 6 H<sub>2</sub>O.—Although this salt may be formed by the action of hydrochloric acid upon the neutral salt, its ready solubility in cold water makes it more conveniently prepared from equivalent quantities of the free acid and the neutral salt. On cooling the concentrated solution, the salt separates in long slender prisms containing six molecules of water. From more dilute solutions, when crystallization begins at ordinary temperatures, the salt separates in well-formed rhombic plates which contain four molecules of water. Not unfrequently both forms appear together, and we have not been able to determine with precision the conditions essential to the formation of either. The long slender prisms effloresce slowly when exposed to the air. When dried by pressure and by short exposure to the air, it gave the following results:—

- I. 0.6298 grm. of the salt lost, at 100°, 0.1056 grm. H<sub>2</sub>O.
- II. 1.7845 grm. of the salt lost, at  $120^{\circ}$ , 0.3055 grm.  $H_2O$ .

	Calculated for	Four	d.
	Ba(C <sub>8</sub> H <sub>3</sub> SO <sub>8</sub> ) <sub>3</sub> . 6 H <sub>2</sub> O	I.	п.
$H_{s}O$	17.22	16.77	17.12

- I. 0.5242 grm. of the salt dried at 100° gave 0.2361 grm. BaSO.
- II. 0.7035 grm. of the salt dried at 120° gave 0.3155 grm. BaSO<sub>4</sub>. III. 0.7629 grm. of the salt dried at 120° gave 0.3420 grm. BaSO<sub>4</sub>.

The rhombic plates did not lose in weight when exposed to the air, and but slowly over sulphuric acid. The air-dried salt gave the following results:—

- I. 4.3735 grm. of the air-dried salt lost, at 105°, 0.5235 grm. H<sub>2</sub>O.
- II. 1.4496 grm. of the air-dried salt lost, at 105°, 0.1762 grm. H<sub>2</sub>O.
- III. 1.6332 grm. of the air-dried salt lost, at 135°, 0.2010 grm. H<sub>2</sub>O.

Calculated for		Found.		
	$Ba(C_8H_2SO_6)_2 \cdot 4H_2O$ .	I.	II.	III.
H <sub>2</sub> O	12.18	11.97	12.16	12.31

- I. 0.6969 grm. of the salt dried at 105° gave 0.3125 grm. BaSO<sub>4</sub>.
- II. 0.6325 grm. of the salt dried at 140° gave 0.2825 grm. BaSO<sub>4</sub>.
- III. 0.5982 grm. of the salt dried at 140° gave 0.2682 grm. BaSO<sub>4</sub>.

	Calculated for	Found.		
	Ba(C <sub>5</sub> H <sub>8</sub> SO <sub>6</sub> ) <sub>2</sub> .	I.	п.	III.
Ba	26.89	26.36	26.26	26.36

Calcic & Sulphopyromucate, CaC<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>.3 H<sub>2</sub>O. — This salt is quite soluble in cold water, and crystallizes in flat concentrically grouped prisms, which slowly effloresce over sulphuric acid.

0.7413 grm. of the salt lost, at 130°, 0.1364 grm. H<sub>2</sub>O.

	Calculated for		
	CaC <sub>2</sub> H <sub>2</sub> SO <sub>2</sub> . 3 H <sub>2</sub> O.	Found.	
$H_2O$	19.01	18.40	

I. 0.5737 grm. of the salt dried at 125° gave 0.3383 grm. CaSO<sub>4</sub>. II. 0.6405 grm. of the salt dried at 125° gave 0.3770 grm. CaSO<sub>4</sub>.

	Calculated for	Found.	
	CaC <sub>s</sub> H <sub>2</sub> SO <sub>6</sub> .	I.	II.
Ca	17.40	17.34	17.31

Plumbic 8-Sulphopyromucate, PbC<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. 2 H<sub>2</sub>O. — This salt is readily soluble in hot water, more sparingly in cold, and crystallizes in clustered needles. The air-dried salt contained two molecules of water.

2.1320 grm. of the air-dried salt lost at 105° 0.1805 grm. H<sub>e</sub>O.

	Calculated for	
	PbC <sub>8</sub> H <sub>2</sub> 8O <sub>6</sub> . 2 H <sub>2</sub> O.	Found.
H,O	8.31	8.47

- I. 0.6682 grm. of the salt dried at 110° gave 0.5085 grm. PbSO<sub>4</sub>.
- II. 0.5046 grm. of the salt dried at 110° gave 0.3837 grm. PbSO<sub>4</sub>.
- III. 1.0150 grm. of the salt dried at 110° gave 0.5570 grm. CO<sub>2</sub> and 0.0660 grm. H<sub>2</sub>O.

	Calculated for		Found.	
	PbC <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> .	I.	II.	III.
Рb	52.14	51.99	51.96	
C	15.16			14.97
H	0.50			0.72

Argentic &-Sulphopyromucate, Ag<sub>2</sub>C<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. — The silver salt is sparingly soluble in cold water, somewhat more readily soluble in hot water, and crystallizes in short thick prisms. The air-dried salt lost slightly in weight when heated at 120°, but the loss was insignificant.

- I. 0.6788 grm. of the salt gave 0.4779 grm. AgCl and 0.3923 grm. BaSO...
- II. 0.5255 grm. of the salt gave 0.8703 grm. AgCl and 0.8028 grm. BaSO<sub>4</sub>.

Calculated for Ag <sub>2</sub> C <sub>3</sub> H <sub>2</sub> SO <sub>0</sub>		Found.	
		I.	п.
Ag	53.21	53.01	53.04
SÖ,	19.97	19.85	19.78

Potassic &-Sulphopyromucate, K<sub>2</sub>C<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. 4 H<sub>2</sub>O. The potassium salt is extremely soluble even in cold water, and crystallizes in long slender prisms, which apparently contain four molecules of water. They effloresce quite rapidly when exposed to the air, and our determinations of the water of crystallization are, therefore, not entirely satisfactory.

- I. 2.4108 grm. of the salt dried by short exposure to the air lost, at 135°, 0.4966 grm. H<sub>2</sub>O.
- II. 0.9701 grm. of the salt dried by pressure only lost, at 100°, 0.2074 grm. H<sub>2</sub>O.
- III. 1.3420 grm. of the salt dried by short exposure to the air lost, at 115°, 0.2775 grm. H<sub>3</sub>O.

Calculated for		Found.		
	K <sub>2</sub> C <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> . 4 H <sub>2</sub> O.	I.	II.	III.
H,O	21.15	20.60	21.38	20.68

- I. 0.5573 grm. of the anhydrous salt gave 0.3608 grm. K<sub>2</sub>SO<sub>4</sub>. II. 0.5035 grm. of the anhydrous salt gave 0.3242 grm. K<sub>4</sub>SO<sub>4</sub>.
- Calculated for Found.

  K,0,0,H,30,. I. II.

  K 29.16 29.07 28.91

Acid Potassic &-Sulphopyromucate, KC<sub>5</sub>H<sub>5</sub>SO<sub>6</sub>. — The acid potassium salt is very soluble in water, and crystallizes in large anhydrous prisms.

- I. 0.8655 grm. of the salt gave 0.3253 grm. K.SO.
- II. 0.8290 grm. of the salt gave 0.3127 grm. K<sub>2</sub>SO<sub>4</sub>.
- III. 0.7694 grm. of the salt gave 0.2879 grm. K<sub>2</sub>SO<sub>4</sub>.

Calculated for		Found.		
	КС <sub>в</sub> Н <sub>3</sub> 8О <sub>в</sub> .	I.	. II.	ш.
K	16.99	16.89	16.93	16.81

Sodic &-Sulphopyromucate, Na,C<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. 5 H<sub>2</sub>O. — The neutral sodium salt is extremely soluble in water, and crystallizes in long slender needles, which appear to contain five molecules of water. The same salt is obtained in the form of fine felted needles by crystallization from dilute alcohol.

- I. 1.5082 grm. of the salt dried by short exposure to the air lost, at 110°, 0.3970 grm. H<sub>2</sub>O.
- II. 1.4198 grm. of the salt recrystallized from dilute alcohol and dried by short exposure to the air lost, at 135°, 0.3773 grm. H<sub>2</sub>O.
- III. 1.0232 grm. of the salt recrystallized from dilute alcohol and dried by pressure only lost, at 135°, 0.2785 grm. H<sub>2</sub>O.

Calculated for		Found.		
	Na <sub>2</sub> C <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> . 5 H <sub>2</sub> O.	I.	II.	III.
H,O	27.61	26.32	26.57	27.22

I. 0.5195 grm. of the salt dried at 110° gave 0.3115 grm. Na<sub>2</sub>SO<sub>4</sub>. II. 0.5592 grm. of the salt dried at 110° gave 0.3357 grm. Na<sub>2</sub>SO<sub>4</sub>.

	Calculated for	Found.	
Na <sub>2</sub> C <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> .		I.	II.
Na	19.49	19.43	19.45

Acid Sodic 8-Sulphopyromucate, NaC<sub>8</sub>H<sub>8</sub>SO<sub>6</sub>. H<sub>2</sub>O.— This salt crystallizes in long slender prisms, which do not lose in weight when exposed to the air or over sulphuric acid.

I. 2.1303 grm. of the air-dried salt lost, at 110°, 0.1658 grm. H<sub>2</sub>O.

	Calculated for	
	$NaC_8H_2SO_6$ . $H_2O$ .	Found.
$H_2O$	7.76	7.78

I. 1.0224 grm. of the salt dried at 110° gave 0.3371 grm. Na<sub>2</sub>SO<sub>4</sub>. II. 0.9498 grm. of the salt dried at 110° gave 0.3154 grm. Na<sub>2</sub>SO<sub>4</sub>.

Calculated for $NaC_0H_0SO_6$ .		Found.	
		I.	II.
Na	10.75	10.69	10.76

- δ-Sulphopyromucamide, C<sub>5</sub>H<sub>2</sub>SO<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>. By acting upon the dry sodium salt of δ-sulphopyromucic acid with phosphoric pentachloride, and expelling at a gentle heat the greater part of the phosphoric oxychloride formed in the reaction, a viscous oil was obtained which did not invite further investigation. It was, therefore, at once converted into the corresponding amide by the action of concentrated ammonic hydrate. The product of the reaction, after recrystallization from boiling water, formed long flat prisms readily soluble in hot water, sparingly soluble in cold water, which melted at 213°.
  - 0.3441 grm. of substance gave 47.2 c.c. moist nitrogen at 27° and under a pressure of 763 mm.
- II. 0.2025 grm. of substance gave 0.2507 grm. BaSO<sub>4</sub>.
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	Calculated for	Found.	
	CgH28O4(NH2)2.	I.	II.
N	14.73	15.18	
S	16.84		17.00

### Action of Bromine.

At ordinary temperatures dry bromine has little or no action upon dry &sulphopyromucic acid. At 100° in sealed tube a complicated reaction ensues, which we have not yet fully investigated. Ordinary dibromsuccinic acid is formed in considerable quantity, and at the same time a small amount of mucobromylbromide, as was shown by the blue color developed in alkaline solution, and by the formation of mucobromic acid melting at 120–121° on heating with water. There was also formed in small quantity a beautifully crystalline substance, sparingly soluble even in boiling alcohol, which contained sulphur, but no bromine. This substance we unfortunately have not yet succeeded in obtaining in quantity sufficient for further study.

In aqueous solution bromine rapidly oxidizes &-sulphopyromucic acid, even in the cold. The final product of the reaction is fumaric acid, and we have hitherto been unable to isolate any intermediate products. It is probable, however, that maleic acid is in fact the first product of the oxidation. If bromine be added to an aqueous solution of the barium salt of the acid, baric sulphate is immediately thrown down; but since the amount of baric sulphate thus formed is slightly less than the theoretical quantity, secondary products containing sulphur are doubtless formed. In the complete oxidation of the acid we have used a slight excess of bromine, and have finished the reaction by gentle heat. The fumaric acid obtained was identified by qualitative tests, and by the analysis of the silver salt.

I. 0.2124 grm. of the salt dried at 120° gave 0.2406 grm. AgBr.

II. 0.2056 grm. of the salt dried at 120° gave 0.2332 grm. AgBr.

Calculated for		For	ınd.
$\mathbf{Ag_2C_4H_2O_4}$ .		I.	II.
Ag	<b>65.46</b>	65.07	65.15

The decomposition with bromine, therefore, takes place in great part according to the equation,

$$C_5H_4SO_6 + 3Br_2 + 4H_2O = C_4H_4O_4 + CO_2 + H_2SO_4 + 6HBr.$$

## Action of Nitric Acid.

The oxidation of  $\delta$ -sulphopyromucic acid with dilute nitric acid takes place but slowly, and even after long boiling with moderately concen-

trated acid the decomposition is far from complete. After boiling for some time with acid of Sp. Gr. 1.20, and evaporation upon the waterbath, fumaric acid was obtained, together with small quantities of oxalic acid. The fumaric acid was identified, as before, by its physical properties, and by an analysis of its silver salt.

0.1508 grm. of the salt dried at 125° gave 0.1710 grm. AgBr.

	Calculated for	
	$Ag_3C_4H_2O_4$ .	Found.
Ag	65.46	65.15

The reaction with concentrated nitric acid is much more interesting, since the sulpho-group is in this way replaced by the nitro-group and the &-nitropyromucic acid of Klinkhardt,\* formed with comparatively little oxidation. This replacement is slowly effected at ordinary temperatures, but rapidly at 100°. Dry sulphopyromucic acid is slowly added to several times its weight of cold fuming nitric acid. The mixture is at first cooled, and the reaction afterward completed by gentle heat. The nitric acid is then partially removed by evaporation, and the nitropyromucic acid, which separates as the solution cools, recrystallized from hot water. For its complete purification we found it necessary to dissolve the acid in a cold dilute solution of sodic carbonate, to extract with ether this alkaline solution, and to recrystallize from hot water the product obtained by the addition of hydrochloric acid. The pale yellow acid thus obtained crystallized in rectangular plates, which melted at 182–183°.

0.4925 grm. substance gave 37.9 c. c. of moist nitrogen at 16° and under a pressure of 748 mm.

	Calculated for	
	C <sub>8</sub> H <sub>3</sub> (NO <sub>2</sub> )O <sub>3</sub> .	Found.
N	8.91	8.82

The ethyl ether of the acid was easily formed by warming its alcoholic solution with concentrated sulphuric acid. It was sparingly soluble in cold alcohol, and crystallized in broad lustrous plates, which melted at 99–100°. Klinkhardt gives the melting-point of the acid as 183°, and of the ether as 101°.

With the 8-nitropyromucic acid is formed in small quantity a neutral substance containing nitrogen, which was obtained by evaporating the ether used in the extraction of the alkaline solution of the crude nitro-

<sup>\*</sup> Journ. pr. Chemie N. F., xxv. 41.

pyromucic acid. The same substance was formed in somewhat larger quantity when we attempted to prepare nitropyromucic acid without isolating the sulphonic acid by the addition of nitric acid to a solution of pyromucic acid in fuming sulphuric acid. The substance dissolved sparingly in boiling water, and crystallized on cooling in clustered prisms which melted at 100-101°. On warming with sodic hydrate a bright yellow color was developed. A filter paper moistened with its alcoholic solution and exposed to the vapors of ammonic sulphide turned yellow at first, then salmon-red. This behavior corresponds closely with that observed by V. Meyer\* and Otto Stadler in the case of nitro derivatives of thiophen. Although from lack of material we have as yet made no analyses of this substance, we shall describe later a dibromdinitrofurfuran,† which was obtained under similar conditions from the By-dibrom-8-sulphopyromucic acid, whose formation leaves no doubt that this substance is in fact aa-dinitrofurfuran. It will be further studied in the future in this Laboratory.

Fusing potassic hydrate converts the &-sulphopyromucic acid into succinic acid, and at the same time more or less oxalic acid is formed. Although we have also made certain experiments concerning the action of fusing sodic formiate, we have as yet reached no satisfactory conclusion, and must therefore postpone all consideration of our results until we have made further investigations.

#### **B-Brom-8-Sulphopyromucic Acid.**

Although we have not succeeded in preparing substitution products directly from  $\delta$ -sulphopyromucic acid, they may readily be made by the action of fuming sulphuric acid upon substituted pyromucic acids. If  $\beta$ -brompyromucic acid is dissolved in three times its weight of fuming sulphuric acid (Sp. Gr. 1.95), no carbonization takes place at ordinary temperatures, and from the diluted solution may be isolated by neutralization with baric carbonate the barium salt of  $\beta$ -brom- $\delta$ -sulphopyromucic acid. The free acid is extremely soluble even in cold water, and crystallizes in radiating needles which deliquesce rapidly in moist air.

Baric β-Brom-δ-Sulphopyromucate, BaC<sub>5</sub>HBrSO<sub>6</sub>. 4 H<sub>2</sub>O. — This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallizes in flat clustered prisms. It is precipitated in the form of fine needles on the addition of alcohol to its aqueous solu-



Berichte d. deutsch. chem. Gesellsch., xvii. 2779.

<sup>†</sup> Page 205.

tion. The air-dried salt contains four molecules of water, most of which it loses over sulphuric acid, the rest at 100°.

I. 1.9130 grm. of the air-dried salt lost, at 100°, 0.2824 grm. H<sub>2</sub>O.

II. 1.1010 grm. of the air-dried salt lost, at 170°, 0.1630 grm. H<sub>2</sub>O.

Calculated for		Found.	
BaCsHBrSO4 . 4 H2O.		I.	II.
$H_2O$	15.06	14.76	14.80

I. 0.3030 grm. of the salt dried at 170° gave 0.1740 grm. BaSO<sub>4</sub>.

II. 0.3293 grm. of the salt dried at 170° gave 0.1886 grm. BaSO.

Calculated for BaC <sub>5</sub> HBr8O <sub>6</sub> .		Found.	
		I.	II.
Ba	33.75	<b>33.76</b>	83.67

The solubility of the salt in cold water we determined according to the method of V. Meyer.

I. 27.6020 grm. of the solution saturated at 21° gave 0.2300 grm. BaSO<sub>4</sub>.

II. 27.9011 grm. of the solution saturated at 21° gave 0.2369 grm. BaSO<sub>4</sub>.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:—

Calcic \$\beta\$-Brom-\delta-Sulphopyromucate, CaC5HBrSO6. 6 H2O. — The calcium salt proved to be extremely soluble even in cold water. The syrupy solution gradually solidified with the separation of long radiating needles. The air-dried salt apparently contained six molecules of water, five of which it rapidly lost over sulphuric acid.

I. 1.2305 grm. of the air-dried salt lost, at 135°, 0.3193 grm. H<sub>2</sub>O. II. 0.4444 grm. of the air-dried salt gave 0.1413 grm. CaSO<sub>4</sub>.

Calculated for		Found.	
	CaC <sub>2</sub> HBrSO <sub>6</sub> . 6 H <sub>2</sub> O.	I,	II,
H <sub>2</sub> O	25.90	25.95	
Ca	9.59		9.35

0.9681 grm. of the salt dried over sulphuric acid lost, at 185°, 0.0519 grm. H<sub>2</sub>O.

Calculated for		
	CaC <sub>8</sub> HBrSO <sub>6</sub> . H <sub>2</sub> O.	Found.
$H_2O$	5.51	5.39

0.4608 grm. of the salt dried at 135° gave 0.1973 grm. CaSO<sub>4</sub>.

Calculated for CaC<sub>e</sub>HBr8O<sub>e</sub> Found.
Ca 12.94 12.60

Plumbic β-Brom-δ-Sulphopyromucate, PbC<sub>5</sub>HBrSO<sub>6</sub>. 4 H<sub>2</sub>O. — The lead salt is freely soluble in hot water, more sparingly in cold water, and crystallizes in flat clustered prisms, or on rapid cooling in clustered needles. The air-dried salt contains four molecules of water, almost the whole of which it rapidly loses over sulphuric acid.

- I. 1.3814 grm. of the air-dried salt lost, at 130°, 0.1758 grm. H<sub>2</sub>O.
- II. 1.9209 grm. of the air-dried salt lost, at 140°, 0.2507 grm. H<sub>2</sub>O.
- III. 0.3442 grm. of the air-dried salt gave 0.1905 grm. PbSO.
- IV. 0.6382 grm. of the air-dried salt gave 0.3530 grm. PbSO<sub>4</sub>.

Calculated for		Found.			
	PbCsHBrSOs . 4 H2O.	I.	II.	III.	IV.
H <sub>2</sub> O	13.14	12.78	13.05		
Pb	37.78			37.80	87.79

Potassic β-Brom-δ-Sulphopyromucats, K<sub>2</sub>C<sub>5</sub>HBrSO<sub>6</sub>. 1½ H<sub>2</sub>O (?). — This salt is readily soluble in cold water, more sparingly soluble in dilute alcohol. It crystallizes in small six-sided plates which are permanent in the air, but which effloresce over sulphuric acid. Two determinations of the water of crystallization made in different preparations agree precisely with each other, but do not correspond well with any simple formula for the salt.

I. 0.8184 grm. of the air-dried salt lost, at 160°, 0.0537 grm. H<sub>2</sub>O. II. 1.4398 grm. of the air-dried salt lost, at 160°, 0.0942 grm. H<sub>2</sub>O.

	Calculated for	Calculated for	Found.	
	K <sub>2</sub> C <sub>5</sub> HBrSO <sub>6</sub> . H <sub>2</sub> O.	K <sub>2</sub> C <sub>4</sub> HBrSO <sub>6</sub> . 1½ H <sub>2</sub> O.	I.	п.
$H_{\bullet}O$	4.93	7.22	6.56	6.55

0.3652 grm. of the salt dried at 160° gave 0.1825 grm. K<sub>2</sub>SO<sub>4</sub>.

	Calculated for	
	K₂C₃HBr8O⊕	Found.
K	22.52	22.44

The connection between this brom-sulphopyromucic acid and the  $\delta$ -sulphopyromucic acid could evidently be proved most neatly and directly by eliminating from it the bromine, and examining carefully the sulphonic acid thus formed. By warming a strongly ammoniacal solution of the barium salt with zinc dust the bromine was quickly removed.

The filtered solution was boiled with a slight excess of baric hydrate until all the ammonia was expelled and the zinc precipitated. The solution was then freed from the excess of baric hydrate by means of carbonic dioxide, and concentrated on the water-bath. On cooling, the solution deposited globular aggregations of colorless crystals, which appeared to be identical with those of baric \(\delta\)-sulphopyromucate. The identity was fully established by analyses of the salt, and by determinations of its solubility in water.

I. 1.5700 grm. of the air-dried salt lost, at 165°, 0.2803 grm. H<sub>2</sub>O.
 II. 0.7309 grm. of the air-dried salt gave 0.4295 grm. BaSO<sub>4</sub>.

Calculated for		Found.	
	BaC <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> . 4 H <sub>2</sub> O.	I.	11.
$H_2O$	18.02	17.85	
Ba	34.34		84.55

0.4947 grm. of the salt dried at 165° gave 0.3505 grm. BaSO4.

	Calculated for	
	BaC <sub>s</sub> H <sub>2</sub> SO <sub>o</sub> .	Found.
Ba	41.90	41.67

- I. 12.0595 grm. of the solution saturated at 21° gave 0.2985 grm. BaSO<sub>4</sub>.
- II. 12.1868 grm. of the solution saturated at 21° gave 0.2989 grm. BaSO<sub>4</sub>.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:—

These results are sufficient to prove that the sulphonic acid formed by the reduction of the  $\beta$ -brom- $\delta$ -sulphopyromucic acid is identical with that obtained directly from pyromucic acid by the action of sulphuric acid.

# Action of Bromine.

Bromine in aqueous solution readily oxidizes \$\beta\$-brom-\$\delta\$-sulphopyromucic acid or its salts. Since the relative position of the bromine and the sulpho-group had already been established, we thought it necessary to do no more than identify the final product of the oxidation. Bromine was added in slight excess to an aqueous solution of the barium salt, and the reaction completed at a gentle heat. The strongly acid solution was filtered from the baric sulphate which had been formed,

and extracted with ether. The ether left on evaporation a white crystalline acid, which softened somewhat at 120° and melted completely at 165°. After two recrystallizations from water the acid melted sharply at 176–177°, and was therefore monobromfumaric acid. The oxidation took place according to the following equation:—

$$C_3H_3BrSO_6 + 8Br_2 + 4H_2O = C_4H_3BrO_4 + CO_2 + H_3SO_4 + 6HBr.$$

# Action of Nitric Acid.

We have made no experiments concerning the action of dilute nitric acid upon β-brom-3-sulphopyromucic acid, since it could safely be assumed that oxidation would ensue as with the 8-sulphopyromucic acid, and that monobromfumaric acid would be formed. It seemed to us, however, of decided interest to act upon the acid with fuming nitric acid, since a bromnitropyromucic acid should then result. brom-8-sulphopyromucic acid was slowly added to three times its weight of fuming nitric acid. The reaction progressed slowly in the cold, more rapidly on warming, and without any considerable oxidation. After the reaction was completed, the greater part of the nitric acid was expelled by gentle heat, the crystalline acid left was dissolved in a dilute solution of sodic carbonate, and the alkaline solution then extracted with ether. Upon evaporation of the ether a small quantity of a neutral oil was left, which gradually solidified. The quantity of the product which we thus obtained was so minute that further investigation was out of the question. The alkaline solution when acidified and again extracted with ether yielded in abundance a crystalline acid which proved to be β-brom-δ-nitropyromucic acid. It was readily soluble in alcohol, ether, or hot benzol, more sparingly in cold benzol. It dissolved freely in hot water, and as the solution cooled it was deposited in long clustered flattened needles, which contained one molecule of water. The anhydrous acid melted at 159-160°. At 100° the acid appeared to sublime slowly.

- I. 1.2492 grm. of the acid crystallized from water lost, at 60°, 0.0911 grm. H<sub>2</sub>O.\*
- II. 0.9980 grm. of the acid crystallized from water lost, at 78°, 0.0740 grm. H<sub>2</sub>O.

Calculated for $C_8H_2Br(NO_2)O_3$ . $H_2O$ .		Found.	
		I.	п.
$H_2O$	7.09	7.29	7.42

A slight mechanical loss renders the result of this determination uncertain in the second decimal place.

I. 0.2065 grm. of the acid dried at 100° gave 0.1652 grm. AgBr.

II. 0.2648 grm. of the acid dried at 100° gave 14.2 c.c. of moist nitrogen at 20° and under a pressure of 763 mm.

	Calculated for		Found.
	C <sub>8</sub> H <sub>2</sub> Br(NO <sub>2</sub> )O <sub>2</sub> .	I.	II.
$\mathbf{Br}$	33.90	34.04	
N	5.93		6.15

This acid will be further studied in this Laboratory. There can be no doubt, however, that, like the nitropyromucic acid of Klinkhardt, it contains the nitro-group in the  $\delta$  position.

# βy-Dibrom-δ-Sulphopyromucic Acid.

By-dibrompyromucic acid dissolves in fuming sulphuric acid without the slightest carbonization, and is converted in a short time into the corresponding sulphonic acid. A large part of our work was done with material made from pure By-dibrompyromucic acid. We subsequently found, however, as will be described more at length later in this paper, that the \$8-dibrompyromucic was but little affected by fuming sulphuric acid if the action were not too long continued, and that the mixture of the isomeric dibrompyromucic acids obtained from pyromucic tetrabromide could therefore advantageously be employed direct. The mixed acids were dissolved in once and a half their weight of fuming sulphuric acid, and the solution diluted with water after the lapse of two or three The \$8-dibrompyromucic acid thus precipitated was removed by filtration, and the solution neutralized as usual by baric carbonate. The small amount of \$\delta\delta\delta\delta\text{ompyromucic acid, or its decomposition} products, which remained in solution, could readily be removed by the recrystallization of the barium salt which was obtained after evapo-Since the separation of the isomeric dibrompyromucic acids is a matter of some difficulty, the preparation of the sulphonic acid in question is thus greatly facilitated. The free acid is very soluble even in cold water, but is more sparingly soluble in ordinary concentrated sulphuric acid. From sulphuric acid it crystallizes in clustered needles, from water it is deposited in broad flat prisms, which are permanent under ordinary atmospheric conditions.

Baric βγ-Dibrom-δ-Sulphopyromucats, BaC<sub>5</sub>Br<sub>2</sub>SO<sub>6</sub>. 5 H<sub>2</sub>O. — This salt is very readily soluble in hot water, more sparingly in cold water. The hot saturated solution solidifies on cooling, with the separation of long silky radiating needles. The air-dried salt contains five molecules of water, a part of which it loses over sulphuric acid.

I. 1.5136 grm. of the air-dried salt lost, at 125°, 0.2422 grm. H<sub>2</sub>O.

II. 1.7684 grm. of the air-dried salt lost, at 160°, 0.2855 grm. H<sub>2</sub>O.

III. 2.5118 grm. of the air-dried salt lost, at 180°, 0.4013 grm. H<sub>2</sub>O.

Calculated for		Found.		
	$BaC_8Br_2SO_6$ . $5H_2O_6$	I.	11.	111.
$H_2O$	15 65	16.01	16.14	15.97

I. 0.5378 grm. of the salt dried at 125° gave 0.2575 grm. BaSO<sub>4</sub>.

II. 0.4688 grm. of the salt dried at 180° gave 0.2243 grm. BaSO<sub>4</sub>.

III. 0.5317 grm. of the salt dried at 180° gave 0.2550 grm. BaSO<sub>4</sub>.

	Calculated for		Found.	
	BaC <sub>5</sub> Br <sub>2</sub> SO <sub>6</sub>	I.	II.	III.
Ba	28.25	28.15	28.13	28.19

The solubility of the salt in cold water we determined in the usual way.

- I. 10.9011 grm. of the solution saturated at 20° gave 0.2170 grm. BaSO<sub>4</sub>.
- II. 11.9609 grm. of the solution saturated at 20° gave 0.2398 grm. BaSO<sub>4</sub>.

The solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt:—

When an aqueous solution of the barium salt is evaporated at 100°, small clear prisms separate, which contain less water than the salt just described. We found it impossible to prepare this salt satisfactorily for analysis, since it at once took up water in the cold. A preparation which was removed from the hot solution and immediately dried by pressure with filter paper gave on analysis the following results:—

I. 1.6161 grm. of the salt lost, at 140°, 0.1767 grm. H<sub>2</sub>O.

II. 0.6265 grm. of the salt gave 0.2665 grm. BaSO<sub>4</sub>.

Calculated for BaC <sub>5</sub> Br <sub>2</sub> SO <sub>6</sub> . 3 H <sub>2</sub> O.		Found.	
		I.	11.
$O_{\mathbf{g}}H$	10.02	10.93	
Ba	25.42		25.01

Plumbic βγ-Dibrom-δ-Sulphopyromucate, PbC<sub>5</sub>Br<sub>2</sub>SO<sub>6</sub>. 4 H<sub>2</sub>O. — The lead salt is readily soluble in hot water, more sparingly in cold, and crystallizes in fine felted needles, which are permanent in the air, but effloresce over sulphuric acid.

- I. 1.4998 grm. of the air-dried salt lost, at 165°, 0.1686 grm. H<sub>2</sub>O.
- II. 1.0386 grm. of the air-dried salt lost, at 165°, 0.1159 grm. H<sub>2</sub>O.
- III. 0.6246 grm. of the air-dried salt gave 0.3015 grm. PbSO<sub>4</sub>.

	Calculated for		Found.	
	PbC <sub>8</sub> Br <sub>2</sub> SO <sub>6</sub> . 4 H <sub>2</sub> O.	I.	11.	Ш
$H_{2}O$	11.48	11.24	11.16	
Pb	<b>33.01</b>			32.98

0.5019 grm. of the salt dried at 165° gave 0.2741 grm. PbSO<sub>4</sub>.

	Calculated for	
	PbC <sub>8</sub> Br <sub>2</sub> SO <sub>8</sub> .	Found.
Pb	87.82	87.32

Argentic βγ-Dibrom-δ-Sulphopyromucate, Ag<sub>2</sub>C<sub>5</sub>Br<sub>2</sub>SO<sub>6</sub>. H<sub>2</sub>O. — The silver salt is sparingly soluble in cold water, more readily in hot, and crystallizes in large rhombic plates.

1.0216 grm. of the air-dried salt lost, at 120°, 0.0339 grm. H<sub>2</sub>O.

	Calculated for	
	$\Delta g_2 C_6 B r_2 S O_6$ . $H_2 O$ .	Found.
$H_{Q}O$	8.09	3.31

I. 0.3016 grm. of the salt dried at 120° gave 0.1520 grm. AgCl.
 II. 0.3021 grm. of the salt dried at 120° gave 0.1522 grm. AgCl.

	Calculated for	Four	d.
	Ag <sub>2</sub> C <sub>8</sub> Br <sub>2</sub> SO <sub>6</sub> .	I.	II.
Ag	38.30	87.93	87.98

Potassic βy-Dibrom-δ-Sulphopyromucate, K<sub>2</sub>C<sub>5</sub>Br<sub>2</sub>SO<sub>6</sub>. H<sub>2</sub>O. — The potassium salt is readily soluble in hot water, more sparingly soluble in cold water. It crystallizes in flat obliquely truncated prisms.

L 1.0634 grm. of the air-dried salt lost, at 135°, 0.0377 grm. H<sub>2</sub>O.

II. 0.5807 grm. of the air-dried salt gave 0.2072 grm. K<sub>2</sub>SO

Calculated for		Found.	
	K <sub>2</sub> C <sub>3</sub> Br <sub>2</sub> SO <sub>4</sub> . H <sub>2</sub> O.	I.	11,
H <sub>2</sub> O	4.05	8.55	
K	17.60		17.58

0.4507 grm. of the salt dried at 135° gave 0.1823 grm. K, SO.

	Calculated for	
	K <sub>2</sub> C <sub>5</sub> Br <sub>2</sub> SO <sub>6</sub> .	Found.
K	18.35	18.16

From the structure of the By-dibrompyromucic acid, which has already been determined by Hill and Sanger,\* it is evident that a sulphonic acid formed from it must of necessity contain the sulpho-group in the d position. It therefore seemed to us of interest to prepare from this By-dibrom-8-sulphopyromucic acid, by the elimination of the bromine, the corresponding sulphopyromucic acid. Should this acid prove to be identical with that made directly from pyromucic acid by means of sulphuric acid, the d position of the sulpho-group in the latter acid would be established with precision. A strongly ammoniacal solution of baric By-dibrom-8-sulphopyromucate was warmed for some time with an excess of zinc-dust. After reduction had taken place the filtered solution was boiled with an excess of baric hydrate until the ammonia had been expelled, and the excess of baric hydrate then removed with carbonic dioxide. The concentrated solution deposited on cooling hemispherical aggregations of colorless crystals, which upon investigation proved to be identical in composition with the baric sulphopyromucate already described, and to have also the same solubility in cold water.

0.6194 grm. of the air-dried salt lost, at 160°, 0.1111 grm. H<sub>2</sub>O, and gave 0.3614 grm. BaSO<sub>4</sub>.

	Calculated for	
18	aC <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> . 4 H <sub>2</sub> O.	Found.
H,O	18.02	17.94
Ba	34.34	34.30

- I. 12.9988 grm. of the solution saturated at 21° gave 0.3169 grm. BaSO<sub>4</sub>.
- II. 13.0993 grm. of the solution saturated at 21° gave 0.3181 grm. BaSO<sub>4</sub>.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt:—

It will be seen that these results prove the identity of this salt with that made directly from pyromucic acid.

# Action of Bromine.

Bromine in aqueous solution readily oxidizes  $\beta\gamma$ -dibrom- $\delta$ -sulphopy-romucic acid or its salts. If a slight excess of bromine is added to an

<sup>\*</sup> These Proceedings, xxi. 181.

aqueous solution of the barium salt, baric sulphate is at once precipitated, and after the reaction is completed by gentle heat ether extracts from the filtered solution dibrommaleic acid. The anhydride formed by sublimation was found to melt at the proper point, 114-115°.

# Action of Nitric Acid.

Diluted nitric acid oxidizes By-dibrom-d-sulphopyromucic acid on beating and forms dibrommaleic acid, whose identity we established through the melting-point of its anhydride, 114-115°. By the action of fuming nitric acid a nitro-acid is formed. The dry acid was slowly added to several times its weight of fuming nitric acid. At first the mixture was cooled, afterwards warmed and the greater part of the nitric acid then expelled by gentle heat. The crystalline product of the reaction was in part an acid quite readily soluble in hot water, and in part a neutral substance which dissolved with more difficulty in boiling water. For the complete separation of these two substances we treated the product with a dilute solution of sodic carbonate and extracted with ether. The alkaline solution was then acidified and the acid extracted with ether. After several recrystallizations from hot water, it formed finely felted yellow needles, which were sparingly soluble in cold water, more readily in hot, and melted at 204-205°. They dissolved freely in alcohol, ether, or in benzol. Analysis showed the substance to be a dibromnitropyromucic acid.

- I. 0.1050 grm. of the acid gave 0.1260 grm. AgBr.
- II. 0.2970 grm. of the acid gave 11.7 c. c. of moist nitrogen at 21° under a pressure of 758 mm.

	Calculated for	
	C <sub>s</sub> HBr <sub>s</sub> (NO <sub>2</sub> )O <sub>3</sub> .	Found.
$\mathbf{Br}$	50.79	51.07
N	4.44	4.47

The mode of its formation shows that this acid must of necessity be the  $\beta\gamma$ -dibrom- $\delta$ -nitropyromucic acid.

The ether which had been used for extracting the alkaline solution of the crude nitro product left, on evaporation, a quantity of a yellow crystalline solid, which was sufficient to enable us to establish its identity by analysis. The substance was sparingly soluble even in hot water, and crystallized on slow cooling in stout prisms, or on rapid cooling and scratching in felted needles. In alcohol it was sparingly soluble; but benzol dissolved it freely, and on standing the solution deposited quite large transparent yellow prisms, which effloresced rap-

idly on exposure to the air. The melting point to the effloresced substance was 150-151°, and the percentage of bromine it contained showed that it was a dibromdinitrofurfuran.

0.2008 grm. of the substance gave 0.2396 grm. AgBr.

 $\begin{array}{ccc} & \text{Calculated for} \\ & \text{$C_4$Br}_3(\text{NO}_3)_3\text{O}. & \text{Found.} \\ \text{Br} & 50.63 & 50.79 \\ \end{array}$ 

The clear crystals deposited from benzol evidently contained benzol of crystallization. They effloresced so rapidly, however, that the exact determination of the combined benzol was somewhat difficult.

0.2611 grm. of the substance rapidly pressed and weighed lost, on standing exposed to the air until the weight was constant, 0.0486 grm. benzol.

 $\begin{array}{ccc} & & \text{Calculated for} \\ & \text{C}_4\text{Br}_5(\text{NO}_2)_2\text{O} \cdot \text{C}_6\text{H}_6. & \text{Found.} \\ \text{C}_6\text{H}_6 & 19.80 & 18.61 \\ \end{array}$ 

Considering the difficulty of such determinations, this result leaves no doubt that this dibromdinitrofurfuran crystallizes with one molecule of benzol. The mode of formation of this substance leaves no possible doubt that it is the aa-dinitro- $\beta\beta$ -dibromfurfuran.

#### B-Sulpho-8-Brompyromucic Acid.

The three sulphonic acids thus far described contain the sulphogroup in the  $\delta$  position, and, in the two cases where the formation of isomeric products is theoretically possible, we have hitherto been unable to prove that any isomeric sulphonic acids are in reality formed. For the preparation of such isomeric products it was, therefore, evidently necessary to start with the  $\delta$ -hydrogen atom otherwise replaced, and the  $\delta$ -brompyromucic acid formed the most convenient material. We found no difficulty in preparing in this way a sulphonic acid, which we have called the  $\beta$ -sulpho- $\delta$ -brompyromucic acid, and from it the  $\beta$ -sulphopyromucic acid itself may be made. Since the brominated acid was of necessity first prepared, and we were able to investigate it more fully, it may be more conveniently first described.

ô-brompyromucic acid dissolves in fuming sulphuric acid without essential decomposition, and after the lapse of some time the formation of the sulphonic acid appears to be complete. On neutralizing the diluted solution with baric carbonate, a barium salt is obtained which is sparingly soluble even in hot water, and which usually persistently

retains a slight yellow or greenish color. The purification of this neutral salt is still further rendered difficult by the fact that a hot saturated solution of the salt deposits little or nothing on cooling, and recrystallization therefore involves the evaporation of comparatively large quantities of liquid. The purification may be more conveniently effected by conversion into the more soluble acid salt, or by preparing the acid salt at the outset. The acid salt may easily be made by dissolving the neutral salt in hydrochloric acid somewhat diluted with water, and removing by recrystallization the baric chloride formed. From a solution of the acid salt the neutral salt may again be precipitated by the addition of baric acetate, or of course by the addition of ammonic hydrate and the necessary quantity of baric chloride. The free acid made from the barium salt by exact precipitation with sulphuric acid forms oblique flat prisms or plates, which deliquesce in moist air.

Baric  $\beta$ -Sulpho- $\delta$ -brompyromucate, BaC<sub> $\delta$ </sub>HBrSO<sub> $\delta$ </sub>. 5 H<sub>2</sub>O. — The barium salt is sparingly soluble in hot or cold water, and crystallizes in clear six-sided, clustered prisms. Its aqueous solution is precipitated by the addition of alcohol. The salt contains five molecules of water, four of which it loses slowly on exposure to the air, or more rapidly when heated to  $100^{\circ}$ .

- I. 2.1588 grm. of the salt dried by short exposure to the air lost, at 162°, 0.3806 grm. H<sub>•</sub>O.
- II. 1.1795 grm. of the salt dried by short exposure to the air lost, at 170°, 0.2010 grm. H<sub>2</sub>O.

Calculated for		Found.	
BaC <sub>5</sub> HBrSO <sub>6</sub> · 5 H <sub>2</sub> O.		I.	II.
H.O	18.14	17.63	17.88

- I. 1.8574 grm. of the salt dried at 100° lost, at 162°, 0.0792 grm. H<sub>2</sub>O.
- II. 0.7262 grm. of the salt dried at  $100^{\circ}$  lost, at  $160^{\circ}$ , 0.0317 grm.  $H_2O$ .

Calculated for		Found.	
BaC <sub>5</sub> HBrSO <sub>4</sub> . H <sub>2</sub> O.		I.	п.
H,O	4.25	4.28	4.37

- I. 0.6945 grm. of the salt dried at 160° gave 0.3980 grm. BaSO<sub>4</sub>.
- II. 0.7840 grm. of the salt dried at 140° gave 0.4500 grm. BaSO<sub>4</sub>.
- III. 0.7825 grm. of the salt dried at 140° gave 0.4495 grm. BaSO<sub>4</sub>.

	Calculated for	Found.		
	BaCsHBrSOs.	I.	n.	ш.
$\mathbf{Ba}$	33.75	83.69	<b>33.75</b>	83.77

We also determined the solubility of the salt in water at ordinary temperatures. Since the hot saturated solution deposited little or nothing on cooling, we prepared the solution by boiling down the hot aqueous solution until the salt began to separate. On cooling this supersaturated solution, abundant crystals were deposited.

- I. 32.6032 grm. of the solution saturated at 20° gave 0.5016 grm. BaSO<sub>4</sub>.
- II. 33.7864 grm. of the solution saturated at 20° gave 0.5194 grm. BaSO<sub>4</sub>.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt:—

Acid Baric β-Sulpho-δ-brompyromucate, Ba(C<sub>5</sub>H<sub>2</sub>BrSO<sub>6</sub>)<sub>2</sub>. 4 H<sub>2</sub>O. — This salt is most easily prepared by dissolving the neutral barium salt in diluted hydrochloric acid. It is readily soluble in hot water, sparingly in cold water, and crystallizes in large well-formed prisms, which appear to be triclinic. The salt loses nothing when exposed to the air, or over sulphuric acid, and the loss at 100° is also insignificant. At 130° it slowly loses in weight, but turns brown and suffers partial decomposition before complete dehydration is reached.

- I. 0.7884 grm. of the air-dried salt gave 0.2456 grm. BaSO.
- II. 0.7804 grm. of the air-dried salt gave 0.2460 grm. BaSO<sub>4</sub>.

Calculated for		<b>F</b> ou	nd.
$Ba(C_8H_2BrSO_8)_3$ . 4 $H_2O$ .		I.	n.
Ba	18.29	18.32	18.53

Calcic β-Sulpho-δ brompyromucate, CaC<sub>5</sub>HBrSO<sub>6</sub>. 2 H<sub>2</sub>O. — The calcium salt is quite readily soluble in cold water, and its solubility is but little increased by heat. It crystallizes in compactly aggregated oblique prisms, which are permanent in the air, and lose but little in weight over sulphuric acid or when heated to 100°.

I. 1.7804 grm. of the air-dried salt lost, at 205°, 0.1767 grm. H<sub>2</sub>O.
 II. 0.6483 grm. of the air-dried salt gave 0.2544 grm. CaSO<sub>4</sub>.

Calculated for CaC <sub>2</sub> HBrSO <sub>6</sub> . 2 H <sub>2</sub> O.		Found.	
		I.	11,
H,O	10.42	9.92	
Ca	11.60		11.54

0.4645 grm. of the salt dried at 200° gave 0.2015 grm. CaSO<sub>4</sub>.
 0.4026 grm. of the salt dried at 200° gave 0.1758 grm. CaSO<sub>4</sub>.

	Calculated for		Found.	
	CaC <sub>5</sub> HBrSO <sub>6</sub> .	•	I.	II.
Ca	12.94		12.76	12.83

Plumbic β-Sulpho-δ-brompyromucate, PbC<sub>5</sub>HBrSO<sub>6</sub>.— The lead salt is tolerably soluble in cold water, and its solubility is but little increased by heat. The salt dried by exposure to the air contains one and a half molecules of water, one molecule of which it retains when dried over sulphuric acid.

- I. 1.5047 grm. of the air-dried salt lost, at 150°, 0.0815 grm. H<sub>2</sub>O, and gave 0.9074 grm. PbSO<sub>4</sub>.
- II. 1.7254 grm. of the air-dried salt lost, at 150°, 0.0925 grm. H<sub>2</sub>O.
  III. 0.5361 grm. of the air-dried salt gave 0.3239 grm. PbSO<sub>4</sub>.

Calculated for		Found.		
	PbC <sub>5</sub> HBrSO <sub>6</sub> . 1½ H <sub>2</sub> O.	I.	II.	m.
H,O	5.37	5.42	5.36	
Pb	41.15	41.20		41.27

1.6958 grm. of the salt dried over sulphuric acid lost, at 150°, 0.0629 grm. H<sub>4</sub>O.

	Calculated for	
	PbC <sub>5</sub> HBrSO <sub>6</sub> . H <sub>2</sub> O.	Found.
H,O	8.64	8.71

I. 0.5894 grm. of the salt dried at 150° gave 0.3743 grm. PbSO<sub>4</sub>. II. 0.6496 grm. of the salt dried at 150° gave 0.4122 grm. PbSO<sub>4</sub>.

Calculated for		Found.	
PbC <sub>5</sub> llBrSO <sub>6</sub> .		I.	II.
$\mathbf{P}\mathbf{b}$	43.49	43.38	43.35

Argentic β-Sulpho-δ-brompyromucate, Ag<sub>2</sub>C<sub>5</sub>HBrSO<sub>6</sub>. 2 H<sub>2</sub>O. — The silver salt is sparingly soluble in cold water, and crystallizes in plates which contain two molecules of water.

1.3888 grm. of the air-dried salt lost, at 115°, 0.0968 grm. H<sub>2</sub>O.

Calculated for Ag<sub>2</sub>C<sub>5</sub>HBrSO<sub>6</sub> . 2H<sub>2</sub>O. Found. H<sub>2</sub>O 6.91 6.97

- I. 0.1715 grm. of the salt dried at 115° gave, on precipitation with HBr, 0.1340 grm. AgBr.
- II. 0.1725 grm. of the salt dried at 115° gave, on precipitation with HBr, 0.1837 grm. AgBr.

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III. 0.4347 grm. of the salt dried at 115° gave, on heating with HNO<sub>2</sub>, 0.1684 grm. AgBr and 0.2082 grm. BaSO<sub>4</sub>.

IV. 0.5100 grm. of the salt dried at 115° gave, on heating with HNO<sub>2</sub>, 0.1980 grm. Ag Br.

	Calculated for	Found.			
	Ag <sub>2</sub> C <sub>5</sub> liBrSO <sub>6</sub> .	I.	II.	III.	IV.
Ag	44.54	44.88	44.53		
SO,	16.53			16.44	
Br	16.50			16.49	16.52

Potassic β-Sulpho-δ-brompyromucats, K<sub>2</sub>C<sub>5</sub>HBrSO<sub>6</sub>. — The potassium salt is very soluble in cold water, and crystallizes in thick rhombic plates which are anhydrous.

I. 0.4510 grm. of the salt gave 0.2247 grm. K<sub>2</sub>SO<sub>4</sub>.
 II. 0.5020 grm. of the salt gave 0.2530 grm. K<sub>2</sub>SO<sub>4</sub>.

Calculated for		Found.	
K <sub>2</sub> C <sub>5</sub> HBrSO <sub>6</sub> .		I.	п.
K	22.52	22.37	22.62

# Action of Bromine.

Bromine in aqueous solution acts with readiness upon  $\beta$ -sulpho- $\delta$ -brompyromucic acid or its salts. The products vary with the conditions chosen. If one molecule of bromine is slowly added to a cold aqueous solution of the barium salt, carbonic dioxide is evolved and baric dibromfurfuran sulphonate is formed together with baric bromide. This reaction is obviously identical with that noticed by Hill and Hartshorn \* in the decomposition of  $\delta$ -brompyromucic acid in alkaline solution by bromine in which aa-dibromfurfuran is formed. If the baric  $\beta$ -sulpho- $\delta$ -brompyromucate is suspended in a little water, and bromine slowly added, the salt at first dissolves and soon after the baric dibromfurfuran sulphonate crystallizes out. From a more dilute solution the salt can readily be obtained by evaporation. In the latter case, the solution is but feebly acid and the yield nearly quantitative.

Baric aa-Dibromfurfuran-β-sulphonate, Ba(C<sub>4</sub>HBr<sub>2</sub>SO<sub>4</sub>)<sub>2</sub>. H<sub>2</sub>O.— This salt is quite readily soluble in hot water, more sparingly in cold water, and crystallizes in pearly scales or plates.

I. 0.8179 grm. of the air-dried salt lost, at 135°, 0.0204 grm. H<sub>2</sub>O.
 II. 0.8833 grm. of the air-dried salt lost, at 125°, 0.0224 grm. H<sub>2</sub>O.

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Calculated for		Found.	
Ba(C <sub>4</sub> HBr <sub>2</sub> SO <sub>4</sub> ) <sub>2</sub> , H <sub>2</sub> O.		I.	11.
H,O	2.35	2.49	2.54

- I. 0.3952 grm. of the salt dried at 135° gave 0.1238 grm. BaSO<sub>4</sub>.
- II. 0.3932 grm. of the salt dried at 135° gave 0.1223 grm. BaSO<sub>4</sub>.
- III. 0.4219 grm. of the salt dried at 125° gave 0.1320 grm. BaSO.

	Calculated for	Found.		
	Ba(C4HBr2SO4)2	I.	II.	III.
Ba	18.40	18.42	18.28	18.40

Potassic aa-Dibromfurfuran-β-sulphonate, KC<sub>4</sub>HBr<sub>2</sub>SO<sub>4</sub>. — The potassium salt can readily be made by the action of bromine upon a slightly alkaline solution of potassic β-sulpho-δ-brompyromucate. It crystallizes in well-formed prisms which are anhydrous.

- I. 0.3725 grm. of the salt gave 0.4090 grm. AgBr, and 0.2540 grm. BaSO<sub>4</sub>.
- II. 0.3329 grm. of the salt gave 0.3649 grm. AgBr, and 0.2283 grm. BaSO<sub>4</sub>.

Calculated for $KC_4HBr_2SO_4$ .		Found.	
		I.	II.
Br	46.49	46.78	46.66
SO <sub>8</sub>	23.25	23.41	23.55

Bromine in aqueous solution readily attacks the salts of the ac-dibromfurfuran-\beta-sulphonic acid; so that, if an excess of bromine is added to a salt of  $\beta$ -sulpho- $\delta$ -brompyromucic acid, only the products of this second stage of the reaction are obtained. The oxidation goes on slowly at ordinary temperatures, more rapidly on warming, and even after treating for a long time at 100° with an excess of bromine no appreciable amount of sulphuric acid is formed. The final product of the reaction is an acid containing the sulpho-group, which we have named, provisionally at least, sulphofumaric acid. The acid itself we found to be extremely soluble in water, and upon evaporating the aqueous solution in vacuo a viscous residue was obtained which did not crystallize even after long standing. The barium, lead, and silver salts of the acid were very sparingly soluble even in boiling water. The calcium and potassium salts, on the other hand, were very soluble even in cold water, and could not be obtained in crystalline form. might have been expected, the strontium salt proved to be more readily soluble than the barium salt, but it did not crystallize well from water. We also found it impossible to prepare an acid salt the properties of which were more favorable to purification. We therefore prepared and analyzed the barium and silver salts.

Baric Sulphofumarate, Ba<sub>3</sub>(C<sub>4</sub>HSO<sub>7</sub>), x H<sub>2</sub>O. — To an aqueous solution of baric β-sulpho-δ-brompyromucate we added a slight excess of bromine, and finished the reaction by the aid of heat. The strongly acid solution thus obtained was partially neutralized by the addition of baric carbonate, the carbonic dioxide expelled by long boiling, and baric hydrate then added to alkaline reaction. In this way a voluminous flocculent precipitate was thrown down, which was dissolved in boiling dilute hydrochloric acid and reprecipitated by ammonic hydrate. Although the baric sulphofumarate was markedly soluble in a solution of ammonic chloride, the analytical results were more satisfactory than when the salt was again precipitated by baric hydrate. The voluminous precipitate, when thoroughly washed and dried by exposure to the air, formed a light, porous hygroscopic mass, which gave us on analysis varying percentages. The salt dried at 130° gave, however, a constant percentage of barium corresponding to that required by a salt with three molecules of water, and even at 200° one molecule of water appeared to be retained. In each case, however, the ratio between the barium and sulphur was found to be as 3 to 2.

0.6486 grm. of the air-dried salt gave, after fusion with Na, CO<sub>3</sub> and KClO<sub>3</sub>, 0.4918 grm. BaSO<sub>4</sub>(Ba) and 0.3310 grm. BaSO<sub>4</sub>(SO<sub>3</sub>).

	Calculated for	
	Ba <sub>2</sub> (C <sub>4</sub> HSO <sub>7</sub> ) <sub>2</sub> . 7 H <sub>2</sub> O.	Found.
Ba	44.52	44.58
SO,	17.34	17.52
	$Ba : SO_2 = 2.97 : 2$	

Here it will be seen that the air-dried salt contained seven molecules of water. This, however, must have been an accidental coincidence, since the same salt after several days further exposure to the air, contained more water.

1.2865 grm. of the air-dried salt lost, at 200°, 0.1686 grm. H<sub>2</sub>O.

	Calculated for	
	$Ba_2(C_4HSO_7)_2 \cdot 7 H_2O_4$	Found.
6 H <sub>2</sub> O	11.70	13.10

0.5471 grm. of the salt dried at 200° gave 0.4706 grm. BaSO<sub>4</sub>(Ba), and 0.3159 grm. BaSO<sub>4</sub>(SO<sub>4</sub>).

	Calculated for	
	Ba <sub>2</sub> (C <sub>4</sub> HSO <sub>7</sub> ) <sub>2</sub> . H <sub>2</sub> O.	Found.
Ba	50.42	50.56
SO <sub>s</sub>	19.63	19.82
	$Ba: SO_3 = 2.98: 2.$	

- I. 1.1659 grm. of the salt dried at 130° lost, at 200°, 0.0480 grm. H<sub>2</sub>O.
- II. 0.4608 grm. of the salt dried at 130° gave 0.3798 grm. BaSO<sub>4</sub>.
- III. 0.5175 grm. of the salt dried at 130° gave 0.4256 grm. BaSO4.

	Calculated for	Found.		
$\mathbf{Ba_g}(\mathbf{C_4HSO_7})_2 \cdot \mathbf{8H_2O}$ .		I.	II.	III.
2 H <sub>2</sub> O	4.23	4.12		
Ba	48.29		48.45	48.35

In the sulphuric acid determinations given above, the baric sulphate was precipitated in the presence of large quantities of sodium and potassium salts. Although it was purified in the usual way before weighing, the results are undoubtedly still somewhat too high.

Argentic Sulphofumarate, Ag<sub>3</sub>C<sub>4</sub>HSO<sub>7</sub>. x H<sub>2</sub>O. — On adding a solution of ammonic sulphofumarate to an excess of argentic nitrate, the silver salt is thrown down as a heavy curdy precipitate, which frequently becomes crystalline on standing. It is very sparingly soluble in cold water, somewhat more readily in hot. The air-dried salt contains water, a part of which at least it loses at 100°. At 110° it loses more rapidly in weight, but decomposition ensues at the same time. A sample of the salt which had been dried for some time at 100°, but which was still losing very slowly in weight, was analyzed with the following results:—

- I. 0.4448 grm. of the salt gave 0.4673 grm. AgBr, and 0.1938 grm. BaSO<sub>4</sub>.
- II. 0.4834 grm. of the salt gave 0.2933 grm. Ag.

Calculated for $Ag_4C_4HSO_7$ . $H_2O$ .		Fou	nd.
		I.	11,
Ag	60.54	60.39	60.67
SO <sub>3</sub>	14.95	14.92	
	$Ag: SO_3:$	= 3.01 : 1.	

The air-dried salt had already lost at 100° about one molecule of water.

1.0317 grm. of the air-dried salt lost, at 100°, 0.0368 grm. H.O.

	Calculated for	
	Ag <sub>4</sub> C <sub>4</sub> HSO <sub>7</sub> . 2 H <sub>2</sub> O.	Found.
1 H,O	3.26	3.57

The air-dried salt, therefore, appeared to contain two molecules of water. The analysis of a second preparation of the air-dried salt gave substantially the same ratio between ailver and sulphur, and yet showed that the salt contained a lower percentage of silver.

0.4680 grm. of the air-dried salt gave 0.3561 grm. AgCl and 0.2009 grm. BaSO<sub>4</sub>.

	Calculated for	
	$Ag_3C_4HSO_7$ . $2H_2O$ .	Found.
Ag	58.59	57.28
SO <sub>8</sub>	14.46	14.78
	$Ag : SO_s = 2.88 : 1.$	

By drying over sulphuric acid the precipitated silver salt, we were unable to obtain it with any more definite or constant percentages of water.

The lead salt is almost insoluble in water or in dilute acetic acid; but we have been unable as yet to obtain any results on analysis which were wholly satisfactory.

There can be no doubt that  $\beta$ -sulpho- $\delta$ -brompyromucic acid is decomposed by bromine in aqueous solution according to the following equations:—

$$\begin{split} &C_{5}H_{2}Br_{5}O_{6}+Br_{2}=C_{4}H_{2}Br_{2}SO_{4}+CO_{2}+HBr.\\ &C_{4}H_{2}Br_{2}SO_{4}+Br_{2}+3H_{2}O=C_{4}H_{4}SO_{7}+4HBr. \end{split}$$

# Action of Nitric Acid.

The decomposition of  $\beta$ -sulpho- $\delta$ -brompyromucic acid with nitric acid we have followed qualitatively. We have been unable hitherto to effect a replacement of the sulpho-group by the action of fuming nitric acid, as we had so readily done with the  $\delta$ -sulphonic acids. In this case, whatever was the strength of the nitric acid, we could only prove the formation of an acid which was identical in its behavior with sulphofumaric acid. Not unfrequently, however, the oxidation had gone further, and oxalic acid was also formed together with sulphuric acid.

We have made a few experiments concerning the action of fusing potassic hydrate upon potassic  $\beta$ -sulpho- $\delta$ -brompyromucate, and have as yet been able to prove the formation of nothing but oxalic acid. While it is doubtful whether any other product but oxalic acid is normally formed, we shall study the reaction further, as well as the action of fusing sodic formiate.

#### **B-SULPHOPYROMUCIC ACID.**

The ammoniacal solution  $\beta$ -sulpho- $\delta$ -brompyromucic acid is reduced without difficulty by zinc dust. A strongly ammoniacal solution of

the barium salt was heated for some time with an excess of zinc dust, the filtered solution boiled with the addition of baric hydrate till ammonia was no longer given off, and the excess of baric hydrate precipitated with carbonic dioxide. The solution thus obtained yielded on evaporation the barium salt of  $\beta$ -sulphopyromucic acid in satisfactory quantity. Since this salt was very nearly if not quite as soluble in cold water as in hot, its purification could most conveniently be effected by conversion into the acid salt, which was readily soluble in hot water, but sparingly in cold water.

Baric β-Sulphopyromucate, BaC<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. 3 H<sub>2</sub>O.—This salt is sparingly soluble in hot water, and the hot saturated solution deposits nothing on cooling. By evaporation *in vacuo* over sulphuric acid, the salt is obtained in clean obliquely terminated plates, which contain three molecules of water.

I. 1.5356 grm. of the air-dried salt lost, at 160°, 0.2156 grm. H<sub>2</sub>O. II. 1.2179 grm. of the air-dried salt lost, at 160°, 0.1707 grm. H<sub>2</sub>O. III. 0.7448 grm. of the air-dried salt gave 0.4571 grm. BaSO<sub>4</sub>.

Calculated for			Found.	
	$BaC_5H_2SO_6$ . $3H_2O$ .	I.	II.	III.
H <sub>2</sub> O	14.18	14.05	14.02	
Ba	35.96			36.08

0.7139 grm. of the salt dried at 160° gave 0.5092 grm. BaSO<sub>4</sub>.
 0.7303 grm. of the salt dried at 160° gave 0.5197 grm. BaSO<sub>4</sub>.

Calculated for BaC <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> .		Found.	
		I.	II.
Ba	41.90	41.94	41.84

If the solution is evaporated at 100°, the salt separates in small clear prisms with oblique truncations, which appear to contain one molecule of water.\* If the salt is removed while the solution is hot, it contains a somewhat lower percentage of water (IV.) than it does when the solution is first allowed to cool (I., II., and III.). In the latter case it undoubtedly contains a slight admixture of the salt containing three molecules of water.

4.2755 grm. of the air-dried salt lost, at 165°, 0.2510 grm. H<sub>2</sub>O.
 2.1345 grm. of the air-dried salt lost, at 165°, 0.1290 grm. H<sub>2</sub>O.



<sup>•</sup> In a preliminary paper (Berichte d. deutsch. chem. Gesellsch., xviii. 2095) the baric β-sulphopyromucate was described as containing but one molecule of water. At that time the salt obtained by evaporation at 100° had alone been analyzed.

III. 0.5901 grm. of the air-dried salt gave 0.3981 grm. BaSO<sub>4</sub>.
IV. 0.8840 grm. of the air-dried salt lost, at 160°, 0.0484 grm. H<sub>2</sub>O.

	Calculated for	Found.			
	BaC <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> . H <sub>2</sub> O.	I.	II.	III.	IV.
H <sub>2</sub> O	5.22	<b>5.87</b>	6.04		5.47
Ba	39.71			39.66	

I. 0.6005 grm. of the salt dried at 165° gave 0.4270 grm. BaSO<sub>4</sub>.

II. 0.6010 grm. of the salt dried at 165° gave 0.4269 grm. BaSO<sub>4</sub>.

Calculated for BaC <sub>s</sub> H <sub>2</sub> SO <sub>©</sub>		Found.		
		I.	n.	
Ba	41.90	41.79	41.76	

In determining the solubility of the barium salt in cold water, we evaporated its solution rapidly until crystals began to appear, and then cooled with constant stirring. Abundant crystals of the salt were thus formed. In order to satisfy ourselves that solutions of constant composition could be obtained in this way, we made four separate determinations.

- I. 16.2601 grm. of the solution saturated at 21° gave 0.2172 grm. BaSO<sub>4</sub>.
- II. 14.4321 grm. of the solution saturated at 21° gave 0.1950 grm. BaSO<sub>4</sub>.
- III. 12.1256 grm. of the solution saturated at 21° gave 0.1646 grm. BaSO<sub>4</sub>.
- IV. 12.7701 grm. of the solution saturated at 21° gave 0.1788 grm. BaSO<sub>4</sub>.

The aqueous solution of barium salt saturated at 21°, therefore, contained the following percentages of the anhydrous salt:—

I.	II.	111.	IV.
1.88	1.90	1.91	1.96

Acid Baric  $\beta$ -Sulphopyromucate, Ba(C<sub>5</sub>H<sub>3</sub>SO<sub>6</sub>)<sub>2</sub>. 3 H<sub>2</sub>O. — This salt may be made by dissolving the neutral barium salt in hydrochloric acid, or, more advantageously, by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It is readily soluble in hot water, more sparingly in cold water, and crystallizes in small obliquely truncated prisms, which are permanent in the air.

- I. 1.4255 grm. of the air-dried salt lost, at 130°, 0.1403 grm. H<sub>2</sub>O.
- II. 1.3386 grm. of the air-dried salt lost, at 135°, 0.1271 grm. H<sub>2</sub>O.
- III. 0.5371 grm. of the air-dried salt gave 0.2193 grm. BaSO<sub>4</sub>.

	Calculated for		Found.	
	$Ba(C_gH_3SO_6)_2$ . 8 $H_2O$ .	I.	11.	Ш.
H,O	9.42	9.84	9.49	
Ba	23.91			24.00

I. 0.3068 grm. of the anhydrous salt gave 0.1378 grm. BaSO<sub>4</sub>.
 II. 0.3128 grm. of the anhydrous salt gave 0.1409 grm. BaSO<sub>4</sub>.

	Calculated for	Found.	
	Ba(CgH <sub>2</sub> SO <sub>6</sub> ) <sub>2</sub> .	I.	II.
Ba	26.39	26.41	26.48

Calcic β-Sulphopyromucate, CaC<sub>3</sub>H<sub>2</sub>SO<sub>6</sub>. 2 H<sub>2</sub>O.—The calcium salt is quite readily soluble in cold water, and separates on evaporation in crusts. By the addition of alcohol to a cold aqueous solution the salt is precipitated in the form of small prisms, which, when dried by exposure to the air, contain two molecules of water.

I. 1.0454 grm. of the air-dried salt lost, at 130°, 0.1444 grm.  $H_2O$ . II. 1.0285 grm. of the air-dried salt lost, at 135°, 0.1415 grm.  $H_2O$ .

Calculated for $CaC_0H_2SO_0$ . $2H_2O$ .		Found.	
		I.	п.
$H_2O$	13.53	13.81	13.74

0.4790 grm. of the anhydrous salt gave 0.2825 grm. CaSO<sub>4</sub>.
 0.4118 grm. of the anhydrous salt gave 0.2425 grm. CaSO<sub>4</sub>.

Calculated for $CaC_gH_gSO_6$ .		Found.	
		I.	п.
Ca	17.40	17.35	17.32

Potassic β-Sulphopyromucate, K<sub>2</sub>C<sub>5</sub>H<sub>2</sub>SO<sub>6</sub>. 2½ H<sub>2</sub>O. — The potassium salt is extremely soluble in water, and crystallizes in long prisms. It separates in the form of fine needles on the addition of alcohol to its aqueous solution.

1.2358 grm. of the air-dried salt lost, at 140°, 0.1788 grm. H<sub>2</sub>O.

	Calculated for	
	K <sub>2</sub> C <sub>8</sub> H <sub>2</sub> SO <sub>5</sub> . 2½ H <sub>2</sub> O.	Found.
H <sub>2</sub> O	14.37	14.47

I. 0.4028 grm. of the salt dried at 140° gave 0.2601 grm. K<sub>2</sub>SO<sub>4</sub>.
 II. 0.4120 grm. of the salt dried at 140° gave 0.2665 grm. K<sub>2</sub>SO<sub>4</sub>.

Calculated for K <sub>2</sub> C <sub>5</sub> H <sub>2</sub> SO <sub>6</sub> .		Found.	
		I.	п.
K,	29.16	28.99	29.04

# Action of Bromine.

We have as yet made but few experiments as to the action of bromine in aqueous solution upon  $\beta$ -sulphopyromucic acid. They have only been sufficient to show that oxidation here follows the same course that it does in the case of other derivatives of pyromucic acid, in which the  $\delta$ -hydrogen atom is unreplaced. At first products are formed which reduce silver energetically in ammoniacal solution; and only after long warming with an excess of bromine is an acid obtained which resembles in its behavior sulphofumaric acid. Three molecules of bromine gave an acid whose barium salt was very readily soluble in water, and which reduced silver on heating. This reaction will be studied more carefully hereafter, with the hope of isolating the aldehyde acid which is doubtless formed.

# Action of Fuming Sulphuric Acid upon βδ-Dibrompyromucic Acid.

By the action of fuming sulphuric acid upon  $\delta$ -brompyromucic acid, we obtained a sulphonic acid which of necessity contained its sulphogroup either in the  $\beta$  or in the  $\gamma$  position. Analogy left little room for doubt that the acid thus formed was in fact a  $\beta$ -sulphonic acid. It seemed to us not impossible that a  $\gamma$ -sulphonic acid could be formed by the action of fuming sulphuric acid upon  $\beta\delta$ -dibrompyromucic acid, which still retains its  $\gamma$ -hydrogen atom. We found, however, that the reaction takes quite a different course, and that no sulphonic acid is formed.

Pure dry βδ-dibrompyromucic acid, melting at 167-168°, was slowly added to several times its weight of fuming sulphuric acid. No visible reaction took place, and after twenty-four hours standing water precipitated the acid apparently quite unchanged. After the lapse of several days decomposition set in, and carbonic dioxide, bromine, hydrobromic acid, and sulphurous dioxide were evolved. was the reaction that two or three weeks were necessary for its completion at ordinary temperatures. When water gave only a slight flocculent precipitate, the bromine was expelled as far as possible with a current of air, and the whole diluted with water. The small quantity of insoluble matter was then removed by filtration, and the aqueous solution thoroughly extracted with ether. The ether left on distillation a white crystalline acid, which, when pressed and dried, melted at 127-128°. The quantity of the acid thus obtained was

about half that of the βδ-dibrompyromucic acid taken. The acid dissolved readily in less than its own weight of water, leaving but the slightest turbidity, and on evaporation it crystallized in colorless prisms, which melted at 129–130°.\* An analysis showed this substance to be monobrommaleic acid.

0.2235 grm. of the acid dried over sulphuric acid gave 0.2161 grm. AgBr.

Calculated for	
C <sub>4</sub> H <sub>3</sub> BrO <sub>4</sub> .	Found.
41.03	41.15

The melting point and the complete and ready solubility of the crude product showed that monobrommaleic was the only essential constituent. The aqueous solution from which the monobrommaleic acid had been extracted with ether was warmed to expel the ether dissolved, neutralized with baric carbonate, and the filtered solution evaporated. A careful examination of the small amount of barium salt thus obtained failed to show that even a trace of a sulphonic acid had been formed.† This result is in accordance with the results of Hill and Sanger,‡ who found that the  $\gamma$ -hydrogen of the  $\beta\delta$ -dibrompyromucic acid could not be replaced by bromine.

<sup>\*</sup> The melting point of monobrommaleic acid is usually given as 128°, and I have frequently determined it myself without noticing that it varies greatly with the time of heating, as is the case with dibrommaleic acid. How great this variation may be can be seen from the following observations, which I made with this one analyzed sample. The acid in thin-walled capillary tubes was dipped into the bath heated to constant temperature, and the time of melting noted.

Temperature of bath.	Minutes before melting
•	_
143	0.17
140	0.5
135	0.83
133	1.3
131	1.5
125	4.5
121	8.0

The melting point, 129-130°, given above was the result of two successive attempts to determine it at the ordinary speed.—H. B. H.

<sup>†</sup> The statement made in a preliminary paper (Berichte d. deutsch. chem. Gesellsch., xviii. 2095), that a sulphonic acid was formed in this reaction, was subsequently proved to be incorrect.

<sup>†</sup> These Proceedings, xxi. 175.

# Action of Fuming Sulphuric Acid upon Tribrompyromucic Acid.

After the experiments just described there could be little doubt as to the action of fuming sulphuric acid upon tribrompyromucic acid. We thought it worth while, however, to make a single experiment in this direction. Tribrompyromucic acid dissolved readily in fuming sulphuric acid, and decomposition quickly ensued at ordinary temperatures, so that the reaction was completed in the course of a day or two. The diluted solution yielded, as the only product of the reaction, dibrommaleic acid, which we recognized by the melting point of its anhydride (114-115°), and by the analysis of its barium salt.

0.5812 grm. of the air-dried salt gave 0.3063 grm. BaSO.

 $\begin{array}{c} \text{Calculated for} \\ \text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2\,\text{H}_2\text{O}. \end{array} \qquad \qquad \text{Found.} \\ \text{Ba} \qquad \qquad 31.78 \qquad \qquad 31.98 \\ \end{array}$ 

#### THEORETICAL CONSIDERATIONS.

The constitution of the various substances described in the preceding pages requires but little discussion. The position of the sulpho-group in the  $\delta$ -sulphopyromucic acid is established not only by the formation of fumaric acid by its oxidation, but also still more conclusively by its formation in the reduction of  $\beta\gamma$ -dibrom- $\delta$ -sulphopyromucic acid, to which of necessity the formula

$$BrC = C - COOH$$

$$O$$

$$BrC = C - SO2OH$$

must be assigned. The close resemblance in structure of this acid to dehydromucic acid,

$$HC = C - COOH$$

$$O$$

$$HC = C - COOH$$

is evident, and the formation of &-nitropyromucic acid from dehydromucic acid as observed by Klinkhardt,\* finds its complete parallel in

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the conversion of this sulphonic acid by the action of nitric acid into βy-dibrom-δ-nitropyromucic acid and aa-dinitro-ββ-dibromfurfuran.



There can be no doubt that the neutral substance formed by the action of fuming nitric acid upon  $\delta$ -sulphopyromucic acid at the same time with the  $\delta$ -nitropyromucic acid is aa-dinitrofurfuran.



The structure of the  $\beta$ -brom- $\delta$ -sulphopyromucic acid is determined by its reduction to  $\delta$ -sulphopyromucic acid, and by its formation from  $\beta$ -brompyromucic acid, the constitution of which has been established by Hill and Sanger.\* The sulphonic acid and the nitro-acid formed from it must be

$$BrC = C - COOH$$

$$\begin{vmatrix} O & BrC = C - COOH \\ O & O \\ H - C = C - SO_2OH & HC = C - NO_2.$$

Concerning the structure of the sulphonic acid formed from  $\delta$ -brompyromucic acid, it is impossible to draw conclusions equally definite. When we bear in mind, however, the fact that bromine, like sulphuric acid, first replaces the  $\delta$ -hydrogen atom of the pyromucic acid, and in acting upon the  $\delta$ -brompyromucic acid thus formed the  $\beta$ -hydrogen alone can further be replaced by bromine, there seems no reasonable doubt that the sulphuric acid in acting upon  $\delta$ -brompyromucic acid also replaces by the sulpho-group the  $\beta$ -hydrogen atom. This view is still further confirmed by the fact that the  $\gamma$ -hydrogen atom of the  $\beta\delta$ -dibrompyromucic acid seems incapable of such replacement. If this view be correct, the sulphonic acid in question has the form

<sup>\*</sup> These Proceedings, xxi. 181.

$$HOSO_{2}C = C - COOH$$
O
 $HC = CBr$ .

In any case, the aa-dibromfurfuran- $\beta$ -sulphonic acid formed from it by the action of bromine has the structure

$$HOSO_2C = CBr$$

$$O$$

$$HC = CBr.$$

#### XIV.

## CONTRIBUTIONS TO AMERICAN BOTANY.\*

#### BY ASA GRAY.

Presented by Sereno Watson, March 14, 1888.

# Notes upon some Polypetalous Genera and Orders.

#### Rutaceæ.

Although nature, by supplying various connecting links, manifestly invites the union of the Simarubaceæ and Rutaceæ in one order, yet the exclusion of the former enables the botanist to define the latter order by its pellucid-punctate or otherwise glandular-dotted foliage and the accompanying aromatic or pungent or acrid qualities. But it is difficult to draw the line.

PHELLODENDRON shows such dots or glands, few and sparse though they be; so it should rather be placed with the Xanthoxylaceous Rutaceæ. Otherwise we shall be forced to discard some of the species of the Tobinia section of Xanthoxylum.

CNEORIDIUM, Hook. f., must more confidently be restored to Rutaceæ. Hooker, in referring it to Simarubaceæ, on account of its resemblance to Cneorum, was not aware that this little shrub exhales the odor of Rue, and that the taste is not "acrid," but pungent; and it is not difficult to see that the leaves, although opaque, have truly and numerously the Rutaceous glands. Occasionally these are manifest in the petals, and they are apparent in the skin of the drupe. Hooker

This short paper is a continuation of the one by Dr. Gray in the last volume of the Proceedings, entitled "Revision of some Polypetalous Genera and Orders precursory to the Flora of North America." It contains the notes which he had prepared to present to the Academy upon the Rutaceæ and Vitaceæ, the revision of which orders he had taken up immediately after his return from England in October last. He had scarcely commenced his study of the genus Vitis of the latter order when his work upon the Flora of North America ceased. [S. W.]

describes the seed as destitute of albumen, the cotyledons as thick and plano-convex. Torrey, correct as far as it goes, wrote: "Embryo curved in thin fleshy albumen." I find the embryo curved almost into a circle, and a very thin stratum of firm albumen, which might be mistaken for a thick tegmen lining the crustaceous testa. What has not been noticed is, that the oval and not very thick cotyledons are longitudinally convolute, in the manner of Cadellia, F. Müller, as figured by him in Fragm. Phyt. ii. t. 12. As Bentham, in Fl. Austral., describes a monocarpellary species of this genus, with basal style, and which has dotless leaves, it seems that this genus is even more than Cneorum allied to Cneoridium, and that the technical character of the order vanishes.

CHOISYA, HBK. The gynæcium is quite incorrectly figured and described by Kunth. It is in DC. Prodr. i. 724 that the correct character "capsula 5-rostrata" first appears; and the next year (1825) Adrien Jussieu, who well describes the pistil, appends to his account, "Fructus (teste Bonpland) capsularis, 5-sulcus, 5-rostratus." Finally. Baillon (Hist. Pl. iv. 471) adds, "Cocci 5, bivalves, endocarpio soluto"; so he must have found at Paris dehiscent fruit, from which the seeds had fallen, for these are still undescribed. I can now add a second species to this genus, and describe the seeds; viz. C. dumosa, Astrophyllum dumosum, Torr. Pacif. R. Rep. ii. 161, and Bot. Mex. Bound. 42, of which we now possess good flowers and fruit, which quite accord with Choisya. The seeds (solitary or rarely in pairs) are reniform, with nearly smooth subcrustaceous testa, and arcuate embryo in thin albumen. There is either a deciduous caruncle, or else a small and definite portion of the thin-cartilaginous endocarp falls away attached to the hilum.

PTELEA. P. pentandra of Benth. Pl. Hartw. is apparently Rhus Toxicodendron. P. aptera, Parry, of Lower California, is very remarkable for its nucumentaceous and turgid fruit surrounded by a very narrow wing or else quite wingless. As Planchon and Triana have stated, De Candolle was quite wrong in adducing Amyris elemifera, L., to P. trifoliata. Catesby's figure is evidently that of an Amyris, probably the small-leaved form of A. maritima, Jacq. (var. angustifolia), which is found on the coast of Florida, although the leaflets are represented as too broad and rounded at base. The habitat "Carolina" is a mistake, and it has no foundation in Catesby's account.

XANTHOXYLUM. Although most authors, including even the classical Endlicher, have adhered to the faulty orthography, Zanthoxylum, yet the correction was made even in Linnæus's day by Miller, and has been adopted by nearly a dozen of the prominent botanists (including Smith, Sprengel, and Lindley); so that, inasmuch as both forms must be given in indexes, it is better to be correct. As well as I can make out, the name Zanthoxylum began with Plukenet (Alm. 396), and in a confusion (his original being the Fustic-wood of Barbadoes) which has resulted in fixing the name of Yellow-wood upon a large genus of trees and shrubs that have no yellow wood or bark, or hardly any. Linnæus in Gen. Pl. refers the genus to Colden (who knew only the northern X. Americanum); but he had much earlier taken up the genus in Hort. Cliff., from Catesby, whose plant is the Carolinian Clava Herculis. In the first edition of the Spec. Plantarum there is no reference to Browne, Hist. Jam., so the West Indian species has no claim whatever to this specific name. information is needed of the Arkansas-Texan form, which has been regarded as a species by Nuttall, Wright, Buckley, Engelmann, &c., and (in Florida) by Shuttleworth, while I can see in it only a variable form, var. fruticosum. There is, perhaps, more doubt as to X. Caribæum, var. Floridanum, the X. Floridanum, Nutt. Sylv. iii. t. 85, which Watson in his Bibl. Index and Curtiss in his distributed sets refer without question to X. Caribæum, Lam., the full synonymy of which is brought together by Triana and Planchon. But the Florida trees, so far as we know, are unarmed; those of Lamarck's species are said to be prickly; the leaflets of the former are mostly fewer, and those near the inflorescence commonly obtuse; there is an early pubescence on the inflorescence and petioles of the former, and no rimose wartiness. But specimens collected by Sargent have foliage on mature sterile shoots quite like specimens from Martinique, some of which show no prickles; Macfadyen's X. elephantiasis is said to be unarmed, and Grisebach does not assign prickles to his X. aromaticum.

AMYRIS, P. Browne. Hooker's suggestion that this genus should be transferred to the Rutaceæ was rightly acted upon by Triana and Planchon in Ann. Sci. Nat. ser. 5, xiv. 320, where some critical remarks are made upon the species. The wrong reference of Amyris elemifera, L., to Ptelea trifoliata by De Candolle is there corrected. Catesby's figure clearly represents a small-leaved form of the West Indian and Florida coast species. But, by some oversight, Triana and Planchon say that from the figure the species vol. XXIII. (N. S. XV.)

is distinguished from all others by its elongated leaflets, narrow at base, rhomboidal, and by its piperiform fruit. Now the leaflets in Catesby's plate are not at all narrowed at base nor rhomboidal, but ovate-lanceolate. Most specimens do accord with this description, more or less, but not the figure. Jacquin's specific names take priority, having been enumerated in 1760, and one of the names, A. maritima, is cited from Jacquin by Linnæus. To this species our Amyris is evidently to be referred, and this name should be preferred, among other reasons, because it was taken up by Linnæus; while the A. sylvatica, Jacq., if distinct, as Triana and Planchon make out, is the larger and thinner-leaved one named by De Candolle A. Plumieri. The syn. of Catesb. ii. t. 33, cited under A. sylvatica by Jacquin, belongs of course to A. maritima. Catesby gives no habitat, and his plant was probably from the Bahamas, certainly not from "Carolina." Why De Candolle described the lateral leaflets of A. maritima as sessile, and why Grisebach made the leaflets of his A. sylvatica glaucous beneath, one cannot find out. We name our forms

AMYRIS MARITIMA, Jacq. A. sylvatica, DC. Prodr., & Griseb. at least mainly. A. Floridana, Nutt., who perhaps mistakenly represents oval fruit in his Sylva. Leaflets mostly broadly ovate or roundish, obtuse or acute or acuminate, shining and bright green both sides, the veins and reticulated veinlets conspicuous.

Var. ANGUSTIFOLIA. Shrub, apparently more maritime; leaflets ovate-lanceolate or rhombic-lanceolate, smaller (an inch or more long), dull or pale in the dried specimens, and venation less conspicuous. — A. elemifera, L. (Catesb. Car. ii. t. 33). A. sylvatica, Jacq., as to syn. Catesb. only. A. maritima, Griseb., at least in part; Triana & Planch. Ann. Sci. Nat. l. c. 324, excl. syn. Near to this is the following: —

A. PARVIFOLIA; a low shrub, collected by Prof. Sargent on the southeastern border of Texas, on the Rio Grande below Brownsville, and probably the same collected by General Eaton and Dr. Edwards in Mexico, near Monterey: leaflets only half or three quarters of an inch long, rhombic-ovate or narrower, obtuse, nearly all crenate or crenulate, dull, and with comparatively inconspicuous reticulation; lateral ones short-petiolulate or subsessile, as is sometimes the terminal one also.

## Vitaceæ.

AMPELOPSIS, Michx. p. p., Torr. & Gray. Landukia and Parthenocissus, Planchon, Ampelid. in Mon. Phan. Prodr. v. 446, 447. Those who can adopt all or most of the ten genera of Planchon's Ampelideæ may with him reserve the name of Ampelopsis for the first and third of Michaux's species; but if they follow the rule of priority, and think that names given by Rafinesque as late as the year 1830 must needs be adopted, they will take up his name of Quinaria instead of Planchon's new-coined name of Parthenocissus, the homonym of Loureiro being a synonym of an older genus. But I am quite unable to distinguish the A. cordata and the A. bipinnata of Michaux, taken along with the tetramerous Cissus (Ampelopsis, Planch.) orientalis, from the genus Cissus. The Ampelopsis quinquefolia, Michx., remains as the proper representative of the genus, and should preserve the name. This was the course taken, in 1838, in Torrey and Gray's Flora of North America, where the genus was first rightly established, and in the Genera Illustrata, where the peculiarities of the disk and of the tendrils were insisted on; and this generic name has adhered to the Virginia Creeper, and to the Japanese and Indian species which go with it. Moreover, Planchon's Parthenocissus appears to be just the same as his Landukia; for A. Landuk, as described by Miquel, and as well as I can make out on a scanty specimen, has just such a disk, or what answers to disk, as has A. tricuspidata. Thus we have a genus well marked by habit, by its peculiar disciferous tendrils for climbing, and by the adnate thickening of base of ovary in place of the free or partly free torus-disk of the other Ampelideæ. It may still be questioned whether the mass of Ampelideæ can be definitely separated from Vitis, and into how many genera divided; but surely Ampelopsis, with the Virginia Creeper as the type, must be admitted as a good genus.

## XV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

# XXIX.— EXPERIMENTS ON THE BLAKE MICRO-PHONE CONTACT.

By George W. Patterson, Jr.

Presented by Charles R. Cross, January 11, 1888.

In the spring of 1887, Mr. H. J. Tucker and I experimented on the contact in the Blake microphone transmitter, with the object of determining, if possible, the relation between the normal pressure at the contact, and the current in the receiver of the telephone, which was placed in the secondary circuit of an induction coil in the usual manner.

In the following pages I shall give a brief description of our apparatus, and some account of our experiments, with the results reached; and in conclusion I shall deduce, from a consideration of the apparatus and the laws of electricity, equations for curves of pressure and current which are similar to those obtained in experiment.

In our laboratory work we had the advantage of a knowledge of the work which had been done in the preceding two years by Messrs. Page, Lewis, and Hopkins, under the direction of Professor Cross, only a portion of which is published.\*

The object of our work being to determine the variations in the secondary undulatory current caused by variations in the normal pressure at the microphone contact, we required some simple way of regulating the contact pressure, — some way, if possible, which would admit of reproducing precisely the same results from the same conditions of pressure and sound. This latter we failed to accomplish satisfactorily.

Having removed the door, including the microphone contact and the mouthpiece, from the transmitter, we fastened it to the table, leaving space between it and the table for an organ pipe (512 complete vibrations per second), which we used as our source of sound.

<sup>\*</sup> See Proc. Am. Acad., vol. xxi. p. 248.

To obtain a sound of constant intensity, we blew the pipe by means of an air blast driven by the engine in the Rogers Building. The air was regulated by two pressure regulators, one allowing part of the air to escape, the other balancing the air pressure by a column of mercury. The height of the mercury could be changed at will.

The pressure in the Blake contact is regulated by the attachment of the carbon electrode to a spring, whose tension is adjusted by a screw. In addition to the spring, which we used for preliminary adjustment, we applied pressure by means of a lever arm carrying a scale-pan at its centre, one end of which rested on the electrode; the other carrying a knife-edge resting on glass, acted as a fulcrum. The scale-pan was covered by a piece of velvet, in order that the addition of weights might cause no jar at the contact. In our experiments we found that any attempt to take off weights had the effect of disturbing the adjustment of the contact to such an extent as to break the series. This same result was frequently brought about by the jarring of the ground from the street traffic.

We used a more powerful induction coil than that in the Blake transmitter. The resistance of its primary was 0.5 ohm, and of its secondary, 899 ohms.

We experimented on various forms of battery with varying arrangements of the cells, to observe the effect of changes in electromotive force and in resistance. The currents to be measured were very small, and consequently some extremely sensitive form of electrodynamometer was required. We used one of the Kohlrausch pattern with movable coils, which we wound of No. 40 (B. & S. gauge) double silk-covered wire. The two outer coils might be used either in parallel or in series with each other, and in either way with the inner (suspended) coil.

This dynamometer, which differed in some of its details from the instrument as ordinarily made by Hartmann, was constructed especially for experiments of this nature by Mr. Otto Scholl, the mechanician of the Laboratory.

The condition of maximum sensitiveness with coils of a given size is obtained by arranging them so that the product of the ampère-turns in the outer and the inner coils is a maximum.

In designing our inner coil, we were limited by the size of the tube in which it turned. This coil we wound with as many turns as possible, giving a resistance of 180 ohms, which was not too large for the best conditions, the resistance of the induction coil being high. We

then wound two outer coils, each of 800 ohms' resistance, which were as large as it was convenient to fit on to the dynamometer.

For maximum sensitiveness, the resistance of the outer coils should be equal to one fourth of the resistance in circuit. The sensitiveness falls off much more rapidly with decrease of resistance below this point, than it does by increase of resistance above this point. The law is represented by the equation

$$Y = \frac{X}{(a+\beta X^2)^2};$$

in which Y is a measure of the sensitiveness; X, the resistance per foot of the wire in terms of the resistance per foot of the wire of the standard coil;  $\beta$ , the total resistance of the standard coil; and a, all other resistance in circuit, about 1,100 ohms.  $\beta X^2$  is the resistance of the outer coil, the resistance of a fixed weight of wire being directly as the square of its resistance per foot. Y is a maximum when  $a = 3 \beta X^2$ .

It will be seen from the above equation, that, if the outer coils are used in series, the resistance, 1,600 ohms, is much too large; if they are used in parallel, the resistance, 400 ohms, is also large; and the instrument is 64 per cent more sensitive with the parallel arrangement. For best effect, the wire of the outer coils should have had a section 91 per cent larger, and the coils should have been used in series, or a section 4 per cent larger, and have been used in parallel. However, we found that if the outer coils were used in parallel, the dynamometer was sufficiently sensitive.

For a suspension, we finally used a platinum wire, 0.004" in diameter, all lighter ones breaking because of the weight of the coil. The length of the wire was about twenty inches. The inner coil carried a vane, swinging in dilute sulphuric acid, by which one connection was made, the other being made by means of the suspending wire. Mercury was not used, as its surface tension would not allow free enough motion of the contact wire. The deflection of the inner coil was read by a telescope and scale, a mirror being fixed to the coil.

As the currents to be measured were alternating, it was necessary to calibrate the electro-dynamometer for alternating currents; for in rapidly alternating currents the inner coil is acted on by the outer coils only, while in direct currents the magnetism of the earth is felt also. Mr. Hopkins in his experiments had inserted a current alternator between the battery and his dynamometer, but found a great deal of trouble from leakage across the insulation. We therefore

sought to calibrate the dynamometer with direct currents, and, by a mathematical consideration of the curve obtained, to construct a curve proper for alternating currents.

In calibrating this dynamometer we met with considerable difficulty, for it was far too sensitive to be put in direct circuit with the most sensitive standard galvanometer, and it could not be placed in a shunt circuit because of the impossibility of determining its equivalent resistance, the inverse electro-motive force of the sulphuric contact entering in as a doubtful element.

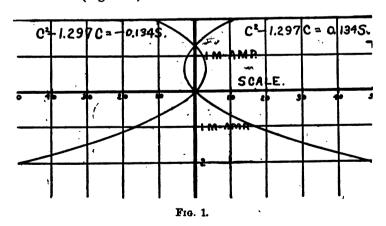
These difficulties were overcome by setting up the dynamometer with the planes of its outer coils east and west, connecting it in series with a very sensitive bell-magnet galvanometer, and observing the corresponding deflections. Series were taken by varying the resistance in circuit, and also reversing the current both at the battery and in the inner coil. The bell-magnet galvanometer having been calibrated by a standard instrument, we computed the currents \* corresponding to the different deflections, and plotted the curves of deflection and current for the dynamometer. These curves were found to be two equal parabolas, whose equations were

$$C^2 - 1.297 C = -0.134 S, (1)$$

and

$$C^2 - 1.297 C = 0.134 S, (2)$$

C being the current in milliampères and S the scale readings in millimeters. (Figure 1.)



A variation of 0.00001 ampère in the current could be measured.

Each parabola was constructed from two series of measurements, in both of which the relative directions of the current in the outer and inner coils were unchanged, each series being represented by a branch of the parabola.

It was next necessary to find the law which the dynamometer would follow for alternating currents.

Taking the forces acting along any line passing through the centre of the coil, we have for the action between the coils a force proportional to the square of the current, and for the action of the earth's magnetism on the suspended coil a force proportional to the current. These two forces are balanced by torsion. Expressed in the form of an equation, this gives  $aC^2 + \beta C = \gamma$ , where C is current and a,  $\beta$ ,  $\gamma$ constants for that position. To obtain the same deflection we might have used a negative current,  $C^1$ , which may be expressed as -nC; then  $a n^2 C^2 - \beta n C = \gamma$ ; from these two equations it follows that  $aC^2 n = \gamma$ , that is, eliminating the earth's action, a steady current of  $C\sqrt{n}$  would produce equilibrium in this position. But, as  $C\sqrt{n}$ is a mean proportional between the arithmetical values of the two currents which produce equilibrium in this position, we have simply to find the mean proportional for each position, and construct a new Solving equations (1) and (2) we get

$$C = \frac{1.297}{2} \pm \sqrt{\left(\frac{1.297}{2}\right)^2 \pm 0.134 S}.$$

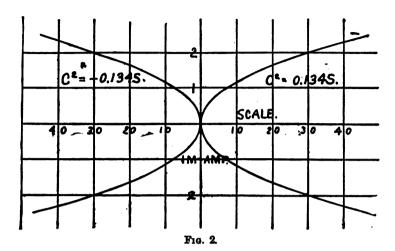
A mean proportional between the values of C for (1) is -0.134 S; for (2) it is +0.134 S. Therefore, the equations for a direct current when the inner coil is free from the earth's effect are

$$C^2 = -0.134 S, (3)$$

and

$$C^2 = +0.134 S. (4)$$

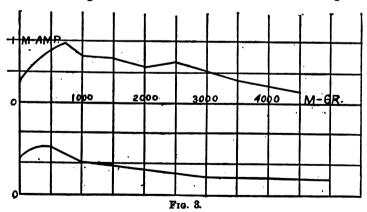
(See Figure 2). In the case of an alternating current, we have a continuous variation in strength; but if we understand by  $C^2$  the mean value of the square of the current, and not the square of its (arithmetically) mean value, which is nearly 20 per cent smaller, when the current variations are of a simple harmonic character, we may use equations (3) and (4) to express variations of current and deflection for alternating currents. In changing from (1) and (2) to (3) and (4), we have made a change in the axes only, the curves being identical.



It will be seen from the demonstration that this transformation of axes without change in the form of curve is peculiar to the parabola.

The calibration being completed, we proceeded to investigate the law of relation between pressure and current, using the Dolbear and chromic acid primary batteries, and the Brush storage battery.

The pressure at the contact was adjusted by the spring until the addition of 25 mgr. would allow sound to be transmitted through the



telephone; the weight was then increased, at first by additions of 250 or 500 mgr., and afterward more rapidly. The deflections, the

<sup>•</sup> In some series the increment was only 25 mgr.

quality, and the intensity of the sound transmitted, were noted. The accompanying plots (Figure 3) and table will serve as examples of the series.

The values given are those of the steady currents, which, in the absence of any magnetic effects from the earth, would give the deflections observed. As the precise form of the variation of the current is uncertain, no better mode of procedure has suggested itself. The columns headed Def., C., and Wt., contain the observed deflections, the calculated currents, and the weights in the pan. These weights should be divided by 2 to obtain the pressure at the contact.

BRUSH STORAGE BATTERY, TWO CELLS IN PARALLEL.

	1.				2.				
Def.	c.	Wt.	Remarks.	Def.	O.	WŁ.	Remarks.		
.85 3.05 5.30 6.45 4.35 3.95 2.55 1.75 1.10 .82	.34 .64 .84 .93 .76 .73 .59 .68 .39	0 250 500 750 1,000 1,500 2,000 2,500 3,500 4,600	Broken sound.  Loud, and beginning to be musical. Loud and good. Lower, and clear.  Wavy.  Good. Low. Very low.	2.20 4.05 4.30 2.10 2.05 .65 .65	.54 .74 .76 .58 .52 .29 .29	0 250 500 750 1,000 8,000 4,000 5,000	Roaring.  Bad.  Loud, and begin- ning to be good. Loud and good. Good, but grow- ing fainter.		

It will be noticed that the current rises very rapidly at first with this increase of pressure. At all points of this rapid rise the sound transmitted is very bad, and there are very frequent breaks with the intensity of sound employed. The maximum is soon reached, at about 1,000 mgr. pressure, and from that point the current falls off gradually. The sound becomes good soon after the maximum current is reached, and as the pressure increases the sound diminishes in intensity but improves in quality. In all our experiments the same form of curve represented the variation of pressure and current, and in all, the best sound was transmitted directly after the maximum current.

I find that this form of curve is in harmony with theory, assuming that the pressure at a microphone contact varies inversely as its resistance. The total resistance in the circuit is a constant plus the resistance of the joint. This may be expressed by the equation

$$R=\alpha+\frac{\beta}{P},$$

R meaning resistance, P pressure, and a and  $\beta$  constants. But

$$C=\frac{\gamma}{R}$$
,

C meaning current, and  $\gamma$  a constant; therefore

$$C = \frac{\gamma P}{aP + B}$$
.

Suppose the sound waves due to the pipe to cause a varying pressure on the contact, whose extreme values are  $\pm \delta$ . The extreme values of the resulting current will be, in each vibration,

$$\frac{\gamma(P+\delta)}{a(P+\delta)+\beta}$$
, and  $\frac{\gamma(P-\delta)}{a(P-\delta)+\beta}$ .

The difference between them will be proportional to the secondary current *I*. The secondary current depends on the rate of change in the primary. This relation may be expressed by the equation

$$I = \Theta\left[\frac{P+\delta}{a(P+\delta)+\beta} - \frac{P-\delta}{a(P-\delta)+\beta}\right] = \frac{2\beta\delta\Theta}{a^2(P^2-\delta^2)+2a\beta P+\beta^2}. (1)$$

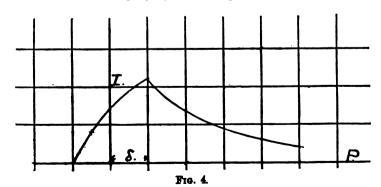
If P is less than  $\delta$ , it is evident that the electrodes will break contact, a minus pressure being impossible. In this case the current at one extreme will be 0 instead of

$$\frac{\gamma(P-\delta)}{a(P-\delta)+\beta},$$

and the secondary current I will be

$$\frac{\Theta(P+\delta)}{a(P+\delta)+\beta}.$$
 (2)

When  $P = \delta$ , these two values for I are identical. The curve obtained by following (2) up to the point  $P = \delta$ , and (1) after that, is similar to the accompanying sketch (Figure 4).



The similarity between the curves B and the curve C shows the close agreement of theory with the results observed.

The first part of the curve, corresponding to equation (2) of incomplete contact, is the curve of imperfect transmission; the last part of the curve, corresponding to equation (1) of complete contact, is the curve of good transmission.

From equations (1) and (2) it will be noticed that the pressure required for good transmission of sound is dependent on the intensity of the sound, good sound being transmitted if  $\delta$  is less than P. The sound in the receiver is loudest when  $\delta$  is nearly equal to P.

In experimenting with electro-motive forces greater than 3 volts, we met with unsatisfactory results. Good sound was not transmitted except under heavy pressure, and all attempts to obtain satisfactory measurements failed on account of the well-known disturbances set up in the microphone by the current itself.

In certain of our experiments the resistance of the primary circuit was diminished by joining a number of cells in parallel. The uniform result was, that the sound transmitted was louder.

The results of our experiments may be summed up as follows: -

The resistance of the primary circuit, and especially that of the battery, should be as low as possible; the pressure at the contact should be no greater than is required to transmit good sound, — that is, it should be a little greater than that required to give the maximum current; with the present form of Blake contact, no electro-motive force greater than 2 volts should be used; and, finally, the contact should be carefully guarded against jarring.

Our work should be considered, not as a complete investigation, but as part of the foundation for future work in the Rogers Laboratory; for our results have been more in the invention of methods than in the use of them. We trust that the work in which we have had a share may be successfully carried out in the future.

ROGERS LABORATORY OF PHYSICS, January, 1888.

## XVI.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXX.—BOILING POINTS OF NAPHTHALINE, BENZO-PHENONE, AND BENZOL UNDER CONTROLLED PRESSURES, WITH SPECIAL REFERENCE TO THERMOMETRY.

BY S. W. HOLMAN AND W. H. GLEASON.

#### Presented January 11, 1888.

THE employment of the melting and boiling of various substances as a means of testing or of graduating thermometers at temperatures above 100° C. is a practice of long standing, especially among chemists. But it will be readily conceded that the results have been in general but roughly approximate, owing to several causes of error, e.g. imperfect purification of substances, faulty apparatus (permitting under or over heating), incomplete systems of thermometry, and errors in the values assumed as the melting and boiling temperatures, these arising, in turn, from causes similar to those just mentioned.

The value of steam as a means of fixing one point on the thermometric scale comes in part from the facts that water does not change composition on boiling at ordinary pressures; that it can be readily obtained in a state of sufficient purity, so that the temperature of its vapor, or rather of a clean thermometer placed in its vapor, can be relied upon as sensibly reproducible under a given pressure; and that this temperature under more than the ordinary range of atmospheric pressure has been measured (by Regnault and Magnus) with sufficient accuracy for thermometric uses. The primary measurement of temperatures above 100° C. is a process of extrapolation from the ice and steam points, and thus possesses the liability to error common to all extrapolation, the magnitude of the error depending upon the method, instruments, and skill employed. It is obvious, therefore, that, whatever be the system of thermometry, a decided gain in accuracy and convenience would accrue to the art of temperature measurement if by

competent investigation other substances could be had which at other temperatures should fulfil the conditions just named as rendering steam so useful.

The investigations in this direction by Prof. J. M. Crafts—in part published \*— contribute far more than any others to the establishment of such fixed reference temperatures. The results of Mills's † measurements of melting points are also important. Independent study of the same substances by various observers is valuable, even when the check results cannot claim all the accuracy of the most elaborate investigations. For it is of material importance to answer in this way for each substance the questions: Is the substance reproducible with sufficient certainty to give wholly independent workers sensibly the same temperature? What is this temperature in absolute degrees (of Thomson scale) as a function of the vapor pressure, errors in thermometric methods being eliminated? Is the substance readily reproducible without great expense?

The following is a brief account of a study of naphthaline, benzophenone, and benzol, undertaken with these points in view, and with special reference to attempting to check the results of Professor Crafts. It is probable that, owing to superior facilities and greater experience, he has obtained results entitled to decidedly greater weight than those which we give. But it is believed that the conditions under which our work was done, and the pains taken in the system of air thermometry, entitle the temperature measurements to consideration.

In designing the apparatus we departed somewhat widely from the published descriptions of Crafts's apparatus in almost all details. Our thermometer contained air dried and freed from CO<sub>2</sub>, while Crafts's contained hydrogen; its bulb was large (about 200 cc.); the substances studied were either commercially obtained or prepared by methods differing from those of Crafts; and the vapor pressures were under control by a regulator, and were extended through a greater range. We have since learned from Professor Crafts that the form of gas thermometer whose description had been published was not invariably employed, but that others of various capacities and forms had been used.

The concordance of our results with those of Professor Crafts for naphthaline (p. 246) is certainly as close as could be anticipated, and is within the limits of error in even the most elaborate use of the



Crafts. Bulletin de la Soc. Chim., xxxix. 196, 277 (1883).

<sup>†</sup> Mills. Phil. Mag., (5,) xiv. 1 (1882).

mercurial thermometer at those temperatures. For benzophenone (p. 247) the accordance is from 0°.3 to 0°.5 C., — a difference possibly arising from errors in thermometry introduced by difficulties met with on our part from somewhat irregular action of the kind of glass which we were forced to employ in our air thermometer bulb, and which rendered the determination of its coefficient of expansion somewhat less satisfactory at this higher temperature than at lower ones. Yet we think the difference too great to be wholly accounted for by thermometric errors.

The results of the investigation may be summarized as follows: ---

1. Naphthaline,  $C_{10}H_8$ , is readily obtainable in a state of sufficient purity to give a reference temperature exact within 0°.1 C. We have found a preparation melting at 79°.4 to 79°.8 to possess a boiling point within the ordinary range of atmospheric pressure (H), expressible by

$$t^{\circ} = 218.07 + 0.0625 (H - 760)$$

where H is the reduced pressure in "normal" millimeters of mercury. Throughout the paper the degrees and pressures may be regarded as "normal," i. e. corresponding to the definitions adopted by the International Committee of Weights and Measures, Trav. et Mém., i. (1881). No reduction for gravity has been made, because the correction at Boston is below the limits of error of this work.

2. Benzophenone,  $(C_6H_5)_2CO$ , is obtainable with some difficulty, and is rather costly. With a melting point of 47°.6 to 48°.0 our determination of the boiling point within the ordinary range of atmospheric pressures is expressible by

$$t^{\circ} = 305.6 + 0.060 \ (H - 760).$$

3. Benzol, C<sub>6</sub>H<sub>6</sub>, is readily obtainable nearly pure. Anhydrous benzol melting at 4°.22 was found to have a boiling point expressible within the ordinary range of atmospheric pressures by

$$t^{\circ} = 80.19 + 0.0455 (H - 760).$$

- 4. The boiling points for pressures down to 80 mm. for naphthaline and benzophenone, and to 360 mm. for benzol, are tabulated on page 247. No attempt has been made to express the vapor pressure as a function of the temperature through these greater ranges by any of the numerous formulæ employed by others for this purpose.
- 5. We regard the actual errors in the final results for the naphthaline and benzol at the atmospheric pressure as under 0°.1, and that for the benzophenone as under 0°.25. The average deviation of the



single observation from the curves upon which the tabular values were interpolated were: naphthaline 0°.1, benzophenone 0°.3, benzol 0°.06.

6. The device used by us for controlling the pressure is easily adjustable, and sufficiently constant to afford, in connection with the substances which we have investigated, a means of obtaining exactly any desired temperature within the range measured. Thus this or a similar apparatus may serve for testing mercurial thermometers at several points, or for maintaining adjusted and known temperatures for other purposes.

#### Air Thermometer.

Primary temperature measurements to be reducible to the absolute scale (Thomson's) must be made by a gas thermometer, and the air The Jolly\* form, in which the thermometer is the most available. closed and open arms of the manometer are connected by a flexible tube, is the most convenient, and was adopted in this work. The difference of level of the mercury surfaces was, however, measured by a special device. Vertically between the two arms of the mercury column is placed a steel millimeter scale of 1.3 cm. square section, and with straight edges. A T-square with double blade is held by the hand firmly against the scale edge, and the blades, which project across the face of the scale, pass, one behind, the other in front of the mercury The square is then slid up or down until the plane of the lower edges of the blades is tangent to the top of the meniscus, just as in setting a barometer vernier. By placing the tubes so that there is a bright light behind them, differences of level of the columns can be read with errors of less than one tenth of a millimeter, the tenths being estimated. The bulb used was about 15 cm. long, 4.5 cm. in diameter, and 0.5 to 1 mm. thick, with a capacity of about 200 cc., and the volume of projecting stem was but 0.64 cc. The glass bulb and tube were continuous over to the three-way cock to which the flexible tube The glass gauge tubes were about 1 cm. inside diameter. The gauges, scale, etc., were carefully protected from heating, and their temperatures obtained by suitably disposed thermometers. The bulb was filled and emptied many times at 100°. The air was thoroughly dried by calcic chloride, sulphuric acid, and phosphoric anhydride, and its carbon dioxide was removed by sodic hydrate. Two determinations of its coefficient of expansion made one before and one after the

<sup>•</sup> Pogg. Ann., Jubelband.

measurements on naphthaline, gave 0.00 366 95 and 0.00 366 87, of which the mean, 0.00 366 91, was employed. Other values are:—

Regnault							0.00 366 82
Magnus							867 10
Jolly .							367 28
Rowland							367 18
Mean							0.00 867 08

With this mean the above value is in so close accordance as to show that the apparatus and coefficient of expansion of glass used must be sensibly correct. The formulæ used in computing a and temperatures was that given by Rowland.\*

The coefficient of expansion of the glass bulb of the air thermometer was obtained by a weight thermometer made from the same piece of tubing. Both bulbs were made of the full diameter of the original tube, and with no further heating than was necessary to close the ends. They were thus both of the same diameter and thickness, and had been subjected to substantially the same treatment. In the computations, the values of the coefficient  $\beta_i$  used for mercury were those of Wüllner's recomputation of Regnault's experiments. Measurements were made in vapor of benzophenone, naphthaline, aniline, and water, a special double-jacketed heater being employed. The results were:—

Temp.	$\beta_t$ used.	ε obtained.		
•	(Wüllner.)	K ODMILIEL		
306	0.00 018 667	0.00 008 004		
806	667	3 012		
218	468	2 895		
18 <del>1</del>	401	2 830		
100	253	2 700		

The values of  $\kappa$  used for the benzol measurements were determined by Mr. W. S. Hadaway, Jr., on glass of the same kind, at temperatures below 100°. The results overlap at 100°, and are sensibly in accord. In some preliminary work, with bulbs carefully annealed before and after having been filled with mercury, values of  $\kappa$  up to 218° were obtained which are in close agreement with the foregoing. The bulbs were all filled by boiling the mercury in them. This mercury and that used in the gauges was redistilled in the laboratory.

The capillary leading from the air thermometer was as fine as possible, and special care was taken to obtain accurately the temperature of the air in the exposed stem of the thermometer.

Proc. Amer. Acad., xv. 98 (1880).
 vol. xxIII. (n. s. xv.)

# Boiling Point Apparatus.

Upon a horizontal circular brass disk of 18 cm. diameter was brazed, with a heavy collar, a vertical thin brass tube 7.8 cm. diameter and 37 cm. high. Eccentrically within this stood a similar tube 6.5 cm. diameter and 34 cm, high, being held in place simply by its weight and by a thin brass collar so near the bottom as to be beneath the surface of the liquid when boiling. Notches cut into the lower edge of the inner tube allowed the vapor formed under this collar to pass into the inner, not into the outer space. A vertical brass tube, open at both ends, about 100 cm. long and 2 cm. diameter, passed through the cover at one side, and extended (by a removable portion) in the outer space of the boiler nearly to the surface of the liquid. served as an escape and condenser tube, and to its top was attached the exhaustion tube when pressures other than the atmospheric were de-Outside this a glass condenser was placed for water circulation when benzol was used; with naphthaline and benzophenone this outer jacket was removed. The height to which the vapor extended in the tube could be ascertained by passing a moist cloth along it, and could be readily maintained nearly constant by adjusting the gas flame beneath the boiler. The cover was a brass casting turned and ground to fit a brass ring brazed to the top of the outer tube of the boiler. was secured to the ring by six screws, and the joint was always very nearly vapor-tight. Through the top were four borings; one nearly central to admit the stem of the air thermometer, three for the insertion of mercurial thermometers to be compared with the air thermom-These borings were closed by perforated screw-plugs, of which the central one was split lengthwise so that it could be placed on the air thermometer stem after this had been passed through the larger hole in the cover. Leakage was reduced to a minimum by an asbestos packing. Thus, when the liquid was boiling, the circulation of vapor was up the inside tube, in which the mercurial and air bulbs were located, down the jacketing space between the tubes, and up into the condenser tube until liquefied, whence it would drip back into the boiler. The depth of liquid in the boiler was from 2 to 5 cm. The sides and top of the boiler were covered with hair felt from one to three inches thick.

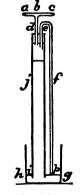
The whole instrument was mounted upon a strong wooden frame in such a way that the cover of the boiler, having the air thermometer rigidly attached to it by a brass bracket, was fixed in place, while the boiler was removable.

For testing mercurial thermometers in the vapor of substances boiling at high temperatures, the following apparatus has been employed. It is similar to the boiler of the larger apparatus. Into the bottom of a thin brass tube, of about 5.3 cm. diameter and 20 cm. high, is brazed a thicker plate. Within this tube stands a shorter tube of about 4.5 cm. diameter notched at the bottom edge, and having a somewhat eccentric collar at about 2 cm. from the bottom, to hold it in place and prevent the vapor from freely rising into the outer jacket. The cover fits with a flange into the top of the outer tube and is split along a diameter. The boring for the insertion of the thermometer is in the centre. Through one half of the cover passes a thin tube about 60 cm. long and 1 cm. internal diameter, projecting about 15 cm. below the cover. This lower portion thus extends nearly to the surface of the liquid in the outer jacket, being placed of course in the larger side of that jacket, and serves as an escape or condenser tube.

# Pressure Regulator.

This has been elsewhere described in full,\* and is shown in the figure. A Richards water-jet aspirator drew air from a b c, and c was

connected with the apparatus to be exhausted. The small glass tube efp was drawn out to an open point at p. As the exhaustion proceeded, the mercury rose in the larger glass tube j and in f, until the level in the open cistern hg fell below p, whereupon the mercury in f would flow over into f, followed by a sudden inrush of air, thus increasing the internal air pressure and causing the mercury to fall somewhat in f and rise at f and the end of f as the end of f and end of f as the end of f as the end of f and f are and f and f are end of f and f are end of f and f and f are end of f and f and f are end of f and f and energy globules would flow continuously through f. To maintain steady action, proper relative sizes of tubes and openings must be discovered,



and some constriction should be placed in ij, and a vessel of large capacity should be present in the circuit. The amount of exhaustion can of course be regulated by the quantity of mercury in the cistern, and by the lengths of the tubes. The pressures were of course measured by a separate mercury column and the barometer.

<sup>\*</sup> Proc. Amer. Acad., xxi. 1 (1885); Technology Quarterly, i. (1886).

#### Instrumental Errors.

The barometer was one which had been compared directly with another which had been studied somewhat by a cathetometer, and by comparison with a Signal Service standard in Boston. Its constant error must have been reduced to a fraction of a millimeter, which, so far as it is constant, would not sensibly affect the temperature measure-Scales were by Brown and Sharpe, of Providence, R. I., and had no errors sensible in this work as compared with a standard scale Thermometers used were corrected. by Prof. William A. Rogers. Those for the more exact work were by Baudin of Paris, and were read to fiftieths of a degree. Pernet's method of thermometry was employed. Calibration and steam exposure corrections were applied. A more extended discussion than has been published, so far as we are aware, as to the precision necessary in the component measurements entering into the air thermometry, was made with a view to best proportioning of parts and their elimination of determinate constant errors.

## Preparation of Substances.

This was done by Mr. Gleason, under the direction of Prof. L. M. Norton and Mr. C. W. Andrews of the Chemical Department of the Institute.

Naphthaline. — The pure product from Kahlbaum, of Berlin, was used without subsequent treatment. Samples were fractionated, and all distilled within 0°.3. These distillates were kept separate, each being divided into as many parts as there were tenths rise in temperature, and the melting points of all were found the same. The range of melting and solidifying points of the naphthaline, as taken from the original package, was 79°.38 to 79°.68; after use through the entire series of observations in the boiling-point apparatus it was 79°.42 to 79°.84.

Benzophenone. — The method of Friedel, Crafts, and Ador \* was at first selected, on account of its apparent simplicity and the ease of production of considerable quantities of the substance in the pure state. For reasons not known, the rate of production was too small; and the process was abandoned in favor of that of Chancel,† namely, the dry distillation of benzoate of calcium. The benzoate was prepared by neutralizing an aqueous solution of benzoic acid with milk of lime.

<sup>\*</sup> Comptes Rendus, xxxv. 673.

<sup>†</sup> Liebig's Ann. d. Chemie u. Pharm., lxxii. 279; lxxx. 285.

When litmus paper gave the neutral reaction, the liquid was filtered hot, evaporated, crystallized, and dried, the mother liquor being evaporated to dryness, and the salt dried. This gave a white product with very little loss. 2500 grams of calcium benzoate were subject to dry distillation, and 820 grams of the crude product were obtained. This liquid was of a dark red color, and 608 grams of it boiled above 200°. The result of fractionation was a straw-colored liquid, which would not solidify by cooling even to -15° C.; but on the addition of a very minute crystal of benzophenone the whole solidified suddenly. This product was again fractionated, and all below 280° rejected. After three recrystallizations from a mixture of alcohol and ether, 500 grams of pure benzophenone were obtained, which, after being dried, melted at 46°.74 to 47°.72; a recrystallization gave the same; but after carrying the benzophenone through the entire series of observations in the boiling-point apparatus, the melting point was 47°.62 to 48°.02, and it solidified at 47°.7, indicating that the initial melting points were probably lowered by presence of alcohol or ether.

Benzol. — The Kahlbaum product was tested for thiophene with isatine, and was shaken with  $P_2O_3$  and distilled. This product melted at  $4^{\circ}.22$ , and was used in the measurements.

## Results.

The direct results obtained will be now given, with deduced formulæ and tables. On page 247 is a table interpolated for each 2 cm. pressure for each substance. In the interpolation for these an application of the method of residual curves greatly facilitated the work. Each table of observations contains two or more series. Columns headed p give measured pressures in millimeters within the boiler; those headed t give the corresponding temperatures measured by the air thermometer. The correction to reduce the air thermometer to absolute scale is beyond the limits of accuracy of this work, and has therefore been omitted.

Naphthaline.

## OBSERVED PRESSURES AND TEMPERATURES.

p.	£.	p.	t.
mm.	0	mm	0
759.8	218.11	84.8	141.94
762.7	218.29	141.4	155.57
713.8	215.20	234.8	172.12
655.9	211.59	836.1	184.88
555.7	204.61	<b>4</b> 61.0	197.02
454.4	196.84	546.7	203.91
852.2	186.39	638.1	210.81
242.5	172.75	711.0	215.00
130.2	152.38	759.0	217.84

Within the limits of 730 and 760 mm. the temperature varies almost directly as the pressure, so that the expression

$$t^{\circ} = 218.07 + 0.0625 (H - 760),$$

serves to give the boiling point of naphthaline under any ordinary atmospheric pressure, H, expressed in normal millimeters of mercury. This and subsequent similar ones may probably be used safely up to 780 mm. The following table serves to compare our results with those of Crafts.

p.	t, Crafts.	t, H. and G.
mm.	•	•
720.89	215.7	215.60
780.31	<b>2</b> 16. <b>3</b>	216.21
740.35	216.9	216.84
750.50	217.5	217.48
760.74	218.1	218.12

[N. B.—In Crafts's original tables appear the erroneous values 753.90 – 217°.8, 755.31 – 217°.9. These pressures should be about 755.60 and 757.31, respectively, as inspection will show.]

## Benzophenone.

## OBSERVED PRESSURES AND TEMPERATURES.

p.	t.	p.	t.
mm.	•	mm.	•
755.1	305.34	104.3	223.60
698.1	801.69	220.2	251.92
644.1	298.08	814.3	265.56
527.7	288.61	445.2	280.98
482.5	280.14	580.5	292.56
318.1	266.52	660.0	299.19
201.2	250.58	789.9	804.76
88 9	219.59	••••	••••

COMPARISON WITH CI	RAFTS'S RESULTS.
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Press.	Crafts.	H. and G.		
mm.	•	0		
732.38	304.3	803.94		
740.06	304.8	308.41		
750.91	805.5	305.05		
760.32	306.1	805.62		

Between 720 and 760 mm. the following expression applies to express boiling point as a function of vapor pressure:—

$$t^{\circ} = 305.6 + 0.060 (H - 760).$$

Benzol.

# OBSERVED PRESSURES AND TEMPERATURES.

p.	t.	<b>p</b> .	t.
mm.	•	mm.	•
769.8	80.65	400.7	60.57
783.6	78.71	851.7	<b>57.34</b>
698.7	77.48	852.9	57.63
660.1	75.70	<b>44</b> 8.8	63.90
608.8	73.11	<b>589.9</b>	72.18
554.7	70.42	652.5	<b>75.52</b>
518.8	68.54	730.1	79.09
454.6	64.78	768.8	80.57

Between 720 and 780 mm. the following expression applies: --

$$t^{\circ} = 80.19 + 0.0455 (H - 760).$$

# Boiling Points from 8 cm. to 76 cm.

Press.	Naphthaline.	Benzophenone.	Benzol,	Press.	Naphthaline.	Benzophenone.	Benzol.
p.	t.	t.	t.	p.	t.	t.	t.
om.	•	0	•	em.	•	•	•
8	140 84	216.0	• • • •	44	195.07	280.4	63.57
10	<b>145.84</b>	222.8	• • • •	46	196.89	282.4	64.90
12	150.54	229.2	••••	48	198.59	284.3	66.20
14	154.86	235.0	• • • •	50	200.24	286.2	67.42
16	158.70	240.4	••••	52	201.85	287.9	68.58
18	162.48	245.1	• • • •	54	208.40	289.7	69.66
20	166.10	249.1	• • • •	56	204.92	291.5	70.70
22	169.4 <b>6</b>	252.6	••••	58	206.42	293.2	71.70
24	172.67	<b>255</b> .8	••••	60	207.88	294.8	72.66
26	175.48	258.7	• • • •	62	209.30	296.4	73.64
28	178.10	261.4	••••	64	210.63	297.8	74.60
80	180.58	264.0	• • • •	66	211.86	299.2	75.57
32	182.93	266.6	••••	68	218.10	800.5	76.58
<b>84</b>	185.17	269.1	• • • •	70	214.35	<b>301.8</b>	77.47
36	187.28	271.6	58.00	72	215.58	803.1	78.87
<b>3</b> 8	189.82	273.9	59.40	74	216.80	804.4	79.28
40	191.29	276.1	60.77	76	<b>2</b> 18. <b>07</b>	805.6	80.19
42	193.20	278.3	62.17	78	••••	••••	81.10

This investigation constituted the thesis work of Mr. Gleason, and the experimental work was very largely conducted by him alone. The expense attending the work has been met in part by an appropriation from the Rumford Fund of the American Academy of Arts and Sciences, in part by the Institute.

ROGERS LABORATORY OF PHYSICS, August, 1887.

## XVII.

## CONTRIBUTIONS TO AMERICAN BOTANY.

## By SERENO WATSON.

#### Presented March 14, 1888.

1. Some New Species of Plants of the United States, with revisions of Lesquerella (Vesicaria) and of the North American species of Draba.

LESQUERELLA; \* new genus of Cruciferæ. Petals spatulate to oblong-obovate, entire. Filaments filiform or rarely dilated: anthers

<sup>\*</sup> The Old World genera of the Vesicaria and Alyssum group are variously understood by European botanists and are very troublesome. The species of Vesicaria upon which all are agreed (V. utriculata, V. Graca and V. glabrescens, the first being one of the two original species) have stout erect leafy stems from a suffrutescent base, glabrous, or pubescent below with appressed 2-parted or somewhat stellate hairs, with large Erysimum-like flowers, very large globose coriaceous pods, nerveless septum, and wing-margined seeds. This is the genus as it is generally accepted on the continent, though Boissier added an imperfectly known species which he considered as probably distinct. If it be thus limited, it is certain that we have no species that can be referred to it. Bentham & Hooker, however, added to it other species with globose pods, separating it (so far as Old World species are concerned) apparently upon that character alone from their Alyssum. These foreign species are (as Prof. Oliver informs me) V. sinuata, Cretica, gnaphalodes, vestita, and probably also V. corymbosa, though this is not included in Prof. Oliver's list. Of these, V. gnaphalodes and V. vestita are so far differentiated from both Vesicaria and Alyssum that Bolssier referred them to distinct genera. V. Cretica is a peculiar suffruticose species with very large coriaceous pods and toothed filaments, usually made a section of Alussum. V. sinuata and V. corymbosa, both referred to Alyssum by Boissier and others, are the two species which most resemble any of our own in habit, indumentum, the form and texture of the pod, etc. The species that are embraced in Alyssum as one polymorphous genus by Bentham & Hooker are separated from their Vesicaria upon the character of the more or less compressed pod, but also often have the filaments toothed or appendaged and the cells of the pod only 1- or 2-seeded. These are divided by Boissier and other prominent botanists into 4 or 5 genera, the question of the retention of which may be left to European botanists to determine. The American species differ from them all, more or

sagittate. Pods more or less turgid, round or ovate or short-oblong (often globose), with nerveless valves and a hyaline septum nerved

less positively. In all our species there is a distinct nerve extending from the apex to the middle of the septum or beyond. The filaments are never toothed or appendaged; the petals are never narrowly unguiculate, and, except in one or two species, are yellow; the ovules are never solitary in the cells, and the pubescence is always more or less stellate or lepidote. Among foreign species the nerved septum is characteristic of the genus Lobularia (Koniga), as limited by the exclusion of Ptilotrichum and by the peculiar appressed 2-forked pubescence; and in these, in addition to the midvein, the septum is covered with a coarse network of veinlets which I have observed in none of ours, and its areolæ are straight and narrowly linear, to which our only approach is in V. globosa. Physaria, which is included by Bentham & Hooker in Vesicaria, is certainly to be separated, and the removal of the remaining American species is, in my opinion, justified by the characters. We, moreover, thus avoid completely the difficulties which beset the arrangement of the Old World genera, and leave the question of our own one that can be answered with comparative ease.

To the species that have hitherto been placed in Vesicaria, I would, therefore, now give the generic name Lesquerella (in preference to reviving Lesquereuxia, the former name of a genus now merged in Siphonostegia), in honor of our venerable and in every way worthy veteran paleontologist and bryologist, Leo Lesquereux. Our one flat-podded species that has been referred to Alyssum (A. Lescurii) appears to differ in no other respect than its less convex valves from a somewhat distinct group of species which can be separated, however, only as a section from the rest. I would arrange the known species of the genus as follows:—

- § 1. ALYSMUS. Not canescent or scarcely so, the pubescence loosely stellate. Winter-annuals, the stems ascending or decumbent: filaments somewhat dilated at base: pods globose; or suborbicular and flattened (in n. 1); cells mostly 6- or 8-ovuled. Tennessee and Texas.
  - \* Seeds margined: cauline leaves mostly auriculate: pods sessile.
    - + Pods flattened (valves but slightly convex), strigose-hispid.
- 1. L. LESCURII. Slender, branching: leaves oblong-ovate or oblong, toothed, the cauline all auriculate: filaments abruptly dilated below: pods 2 or 3 lines long, orbicular to broadly elliptical; style not a line long; cells 4-ovuled; septum dense.—Alyssum Lescurii, Gray. Near Nashville, Tenn.
  - + + Pods globose, glabrous.
- 2. L. GRANDIFLORA. Rather finely pubescent: lower leaves oblanceolate, sinuate or sinuate-pinnatifid, the upper oblong to oblong-lanceolate: petals obovate: filaments narrowed gradually above the base: pods suberect on divaricate pedicels; style a line long or less. V. grandiflora, Hook. V. brevistyla, Torr. & Gray. Middle Texas, from the Gulf to Red River.
- 8. L. AURICULATA. More hirsute with spreading hairs: petals narrower: filaments abruptly and broadly dilated at base: pods slightly narrowed at base.

  —V. auriculata, Engelm. & Gray. San Felipe, Texas (Lindheimer).

from the apex to the middle, several- to many-seeded, sessile or stipitate; stigma flat-capitate, entire or lobed. Seeds rounded, flat, mar-

## \* \* Seeds immarginate; leaves not auriculate.

- 4. L. LASIOCARPA. Finely pubescent: leaves coarsely toothed or pinnatifid, oblanceolate to oblong: petals obovate: pods hirsute, sessile, the stout style half as long. V. lasiocarpa, Hook. Ringgold Barracks, Texas; Tamaulipas, Mexico.
- 5. L. DENSIFLORA. Finely pubescent and somewhat canescent: leaves entire or sparingly repand, oblanceolate: petals broadly spatulate: fruiting raceme often short and crowded; pods glabrous, substipitate, the very slender style as long. V. densiflora, Gray. Central Texas.
- § 2. LESQUERELLA, proper. Canescent throughout with fine appressed and often compact stellate pubescence or lepidote: leaves not auriculate-clasping: filaments filiform or linear-subulate: seeds immarginate.
  - \* Ovary and pod finely pubescent, sessile or very nearly so.
- Pods ovate or oblong or oblong-ovate: biennials or perennials with simple stems.
- → Pods ovate to oblong ovate, acute or acutish, somewhat compressed (the valves less convex toward the apex), erect on spreading or ascending pedicels: pubescence compact and rarely distinctly stellate. Western species.
- 6. L. OCCIDENTALIS. Caudex usually simple: leaves oblanceolate, coarsely sinuate-dentate, the cauline spatulate, entire: pods oval, acutish, 8 or 4 lines long; style 2 lines long; cells 4-ovuled. V. occidentalis, Watson, Proc. Am. Acad. 20. 353. Oregon and Northern California.
- 7. L. Kingii. Leaves entire, the lower ovate, petiolate, the cauline spatulate: pods oblong-obovate, acute, 2 or 3 lines long; style a line long; cells 2-4-ovuled.—V. Kingii, Watson, l. c. Northern Nevada; Lassen's Peak.
- 8. L. ALPINA. Dwarf, usually cespitose and multicipital; stems slender: leaves entire, narrow, linear to linear-oblanceolate: petals spatulate with a broad base: pods oblong-ovate, acute, compressed, 2 lines long; style about as long; cells 2-4-ovuled; septum sometimes perforate. V. alpina, Nutt. Cypress Hills, Canada, to Colorado and Montana.

Var. INTERMEDIA. Stems stouter: flowers larger, the oblong sepals  $2\frac{1}{2}$  to 4 lines long, and the petals more narrowly spatulate: pods ovate-elliptical; cells 4-ovuled. —V. alpina, Gray, Pl. Fendl. 9. New Mexico to southern Colorado and Utah.

- 9. L. ARIZONICA. See page 254.
- → → Pods oblong or oblong-ovate, not compressed or slightly so, erect on
  usually divaricate curved pedicels. Rocky Mountains.
- 10. L. MONTANA. Pubescence often evidently stellate; caudex rarely branched: leaves oblanceolate, the radical often subovate on slender petioles and obscurely toothed: petals spatulate: pods 3 lines long, with long slender style; cells 4-8-ovuled. V. montana, Gray. Northern Colorado and southern Wyoming, near and on the mountains.
- L. Montevidensis. Compactly lepidote: leaves narrowly to linearoblanceolate, entire or repandly dentate: flowers large: pods elliptical, 3 lines

ginless or rarely narrowly margined. Cotyledons accumbent. — Low caulescent annuals or perennials, with stellate often dense or white-

long, the style a line long; cells 4-ovuled. — V. Montevidensis, Eichl. Fl. Bras. 131. 302, t. 67, f. 2. Brazil; the only South American species.

- ++ ++ Pods elliptical, somewhat obcompressed, acute or obtuse, erect on spreading pedicels: pubescence compactly lepidote. Arizona and Mexico. (Abnormal species.)
  - 12. L. (?) WARDII. See page 255.
  - 13. L. (?) CINEREA. See page 255.
- 14. L. (?) ARGENTEA. Leaves oblanceolate to spatulate, toothed or entire: pods elliptical, obtuse, 3 lines long; style a line long; cells 6-8-ovuled. V. argentea, Schauer, Linnæa, 20. 720. Mexico.
  - ← ← Pods globose, or nearly so, and obtuse (acutish in n. 15).
    - Annual or sometimes biennial. Southern.
- 15. L. GLOBOSA. Pubescence dense, evidently stellate; stems slender, often branched: leaves oblong-spatulate to linear-oblanceolate above, entire or sparingly toothed: pods on wide-spreading pedicels, a line in diameter; style longer; cells 2-ovuled. V. globosa, Desv. V. Shortii, Torr. Tennessee to eastern Missouri.
- 16. L. Berlandieri. Pubescence often somewhat sparse; stems slender, often branched: leaves ovate-lanceolate to oblanceolate, lyrately pinnatifid below, repandly toothed above: pods globose or ellipsoidal,  $1\frac{1}{2}$  to  $2\frac{1}{3}$  lines long; style as long; cells 4-6-ovuled. V. Berlandieri, Gray in herb. Near Matamoras and at San Fernando, Tamaulipas (Berlandier).
  - 17. L. PALMERI. See page 255.
    - ↔ Biennial or sometimes perennial. Northern.
- 18. L. LUDOVICIANA. Pubescence evidently stellate or compact below; caudex and stems usually simple: leaves narrowly oblanceolate to linear, mostly entire: pods pendulous on the recurved pedicels, 1½ to 2½ lines long; style about as long; cells 4-6-ovuled.—V. Ludoviciana, DC. Minnesota and central Dakota to Nebraska and northeastern Colorado; northern Arizona (Palmer).

Var. ARENOSA. Low and very slender, with shorter narrow leaves. — V. arenosa, Rich. V. arctica, Hook. Bot. Mag. t. 2882. Saskatchewan region.

- 19. L. DOUGLASII. See page 255.
- \* \* Ovary and pod glabrous (or pubescent in nos. 27 and 31), not at all compressed.
- + Pods oblong or pyriform, substipitate, on long ascending pedicels. Arkansan annuals.
- 20. L. REPANDA. Pubescence finely and usually sparingly lepidote-stellate: leaves from lyrately pinnatifid to linear-spatulate and entire: ovary oblong, acutish, somewhat narrowed to a very short stipe; style about as long; cells 4-ovuled (mature fruit unknown).— V. repanda, Nutt. Banks of Red River (Leavonworth).
- 21. L. NUTTALLII. Like the last, but radical leaves and flowers unknown: pods broadly pyriform, somewhat constricted above the abrupt base, 2\frac{1}{2} lines

lepidote pubescence, and entire or repandly toothed leaves. Flowers yellow (white or rose-colored in one or two species). Pods much

long, shortly stipitate; style 1 or 2 lines long; cells 6-8-ovuled. - V. Nuttallii, Torr. & Gray. Prairies of Red River (Leavenworth).

- + + Pods globose. Southwestern, except n. 81.
- Pods pendent on recurved pedicels, sessile or scarcely stipitate.
  - = Flowers white or rose-colored.
- 22. L. PURPUREA. Biennial or perennial, the caudex simple or branched; pubescence fine, scattered, or more or less compact on the lower leaves: leaves oblanceolate, the lower often coarsely repand or subpinnatifid: pods rarely ascending, 1½ to 3 lines broad; style a line long or less; cells 2-6-ovuled.—

  V. purpurea, Gray. Western Texas to Arizona and northern Mexico.
- 23. L. PALLIDA. Annual, finely and rather sparingly scurfy: leaves oblanceolate, repand: pods shortly stipitate, 2 lines broad; style a line long; cells 6-ovuled. V. pallida, Nutt. San Augustin, eastern Texas (Leavenworth). Perhaps a form of the next.
  - = = Flowers yellow.
- 24. L. RECURVATA. Annual, thinly pubescent: leaves entire, oblong-oblanceolate or -spatulate, short: pods sessile, 1 or 2 lines broad; style about as long; cells 2-4-ovuled. — V. recurvata, Engelm. V. angustifolia, Scheele, in part. Central Texas.
  - ++ ++ Pods suberect on ascending or curved pedicels.
- = Annual (rarely biennial?), usually branched: pods often stipitate. (Very closely allied species.)
- 25. L. LINDHEIMERI. Pubescence very fine or compactly lepidote; stems erect or ascending: leaves oblong- to narrowly oblanceolate, repand or dentate: pods 2 lines broad; stipe short; style rather shorter than the pod; cells 6-8-ovuled. V. Lindheimeri, Gray. Texas.
- 26. L. GRACILIS. Pubescence very fine, usually scanty; stems slender and usually lax: leaves narrowly oblanceolate, entire or sparingly repand: pods stipitate, 1½ or 2 lines broad, on slender often elongated pedicels; style nearly or quite as long; cells 4-6-ovuled. V. gracilis, Hook. V. polyantha, Schlecht. Central Texas to Kansas.
- Var. sessilis. Pods sessile. V. angustifolia, Gray, Pl. Wright. 2.13, in part. Texas (848 Wright; 326 Lindheimer?).
- 27. L. GORDONI. Pubescence somewhat coarser; often low: leaves linear-oblanceolate, entire or rarely repand: pods stipitate, 2 lines broad; style shorter; cells 6-ovuled. V. Gordoni, Gray. Extreme western Texas to New Mexico and Arizona. Very near the last.
- Var. SESSILIS. Pods sessile or nearly so and often pubescent. V. angustifolia, Gray, l. c. in part. Same range.
- 28. L. ANGUSTIFOLIA. Finely lepidote: lower leaves lyrate-pinnatifid, the cauline narrowly linear and petiolate: pods sessile, 2 to  $2\frac{1}{2}$  lines broad; style somewhat shorter; cells 2-ovuled.—V. angustifolia, Nutt. Prairies of Red River, Arkansas (Leavenworth, Nuttall).

compressed in one species, and somewhat so toward the apex in a few others; obcompressed in some doubtful species. *Vesicaria*, Auct., as to American species, excluding *Physaria*.

LESQUERELLA ARIZONICA. Dwarf densely cespitose multicipital perennial, with compact finely stellate or lepidote pubescence: leaves narrowly oblanceolate, entire: flowers rather large, the sepals  $2\frac{1}{2}$  lines long or less; petals with a very broad undulate claw, rounded above: pods broadly ovate, somewhat compressed, acute, pubescent, sessile, the cells 4-ovuled; style a line long or more. — Arizona; near Prescott (16 Palmer, 1876), near Williams Station (4188 Lemmon), at Peach Springs (4177 Lemmon, 64 Jones), and at Mokiak Pass (43 Palmer, 1877).

- = = Biennial or usually perennial (often fruiting the first year): pods sessile, or nearly so, on ascending or spreading pedicels.
  - Pubescence evidently stellate.
- 29. L. ENGELMANNI. Pubescence dense; caudex usually much branched; stems often dwarf, usually simple: leaves ovate and petiolate to linear-oblanceolate, or the upper linear-spatulate, entire or slightly repand: raceme usually short: pods substipitate, 3 lines broad; style as long; cells 6-8-ovuled. V. Engelmanni, Gray. Central Texas to western Kansas and southeastern Colorado.
- 80. L. ARGTREA. Pubescence more or less dense; caudex often simple and apparently annual; leafy stems decumbent or procumbent: leaves ovate and petiolate to narrowly oblanceolate, entire or repand; petals often turning purple: pods sessile, in a long raceme, 2 to 2½ lines broad; style as long or shorter; cells 6-10-ovuled. V. argyrea, Gray. Southwestern Texas and northeastern Mexico.
  - ∞ ∞ Pubescence compactly lepidote, rarely evidently stellate.
- 31. L. ARCTICA. Caudex and stems usually simple, low: leaves spatulate or narrowly oblanceolate, entire: pods 2½ to 3 lines broad; style a line long or less; cells 6-ovuled; septum perforate. —V. arctica, Richards. West Greenland and Arctic Coast to the Mackenzie River.
- Var. Purshii. Pod somewhat pubescent; septum complete. Anticosti Island (Shepherd, Macoun); "Canada" (Pursh, in Herb. Torr.).
- 82. L. FENDLERI. Usually evidently perennial and caudex much branched, often dwarf; stems simple: leaves numerous, entire, mostly narrowly linear-oblanceolate: pods in a dense usually short raceme, 2 or 3 lines long, sometimes ellipsoidal or acutish; style usually as long; cells 10-16-ovuled. V. Fendleri and V. stenophylla, Gray. Western Texas and southern Colorado to Arizona and northern Mexico.
- 33. L. SCHAFFNERI. Caudex simple; stems ascending or decumbent: leaves linear- to oblong-oblanceolate or spatulate, entire or repand: petals turning purple: pods subovate, 1½ to 2½ lines long; style half as long; cells 6-ovuled.— V. Schaffneri, Watson, Proc. Am. Acad. 17. 320. San Luis Potosi, Mexico.

LESQUERELLA PALMERI. Pubescence dense, stellate-lepidote; caudex simple, apparently biennial, the simple stems a foot high or more: basal leaves narrowly oblanceolate, repand, the cauline narrower and mostly entire: petals spatulate, 3 lines long: pods pubescent, ovate-globose to broadly ellipsoidal, erect on long spreading or ascending pedicels; style as long as the pod; cells 2-4-ovuled.—Arizona (Palmer, 1872; cult. at Washington); Topo cañon, Lower California (C. R. Orcutt, 1884).

LESQUERELLA DOUGLASII. Resembling L. Ludoviciana, but the pods smaller, obovate and very obtuse, erect upon the spreading pedicels, and the cells only 2-ovuled: lower leaves sometimes ovate upon a narrow petiole. — Vesicaria Ludoviciana, Hook. Fl. Bor.-Am. 1. 48, as to habitat; Torr. Bot. Wilkes, 232. On the Columbia River east of the Cascade Mountains (Wilkes, Lyall, Suksdorf); Wallowa Mountains, eastern Oregon (Cusick). First collected by Douglas, but locality not given.

LESQUERELLA (?) WARDII. A procumbent and very compactly lepidote biennial (?), with short stems; radical leaves round-ovate on slender petioles, the cauline short, linear- to obovate-spatulate: pods elliptical, somewhat obcompressed, acute or acutish, the valves very convex,  $1\frac{1}{2}$  to  $2\frac{1}{2}$  lines long, erect on short spreading pedicels; septum oblong; cells 2-4-ovuled; style a line long or more: seeds somewhat turgid and irregular, the long radicle more or less curved to one side.— Arizona, on the Aquarius Plateau, at 11,000 feet altitude (L. F. Ward, 1875). An abnormal species.

LESQUERELLA (?) CINEREA. Like the last in habit: sepals narrow, 8 lines long; petals 4 lines long, with a very broad undulate claw somewhat contracted below the rounded blade: ovary elliptical, acute, obcompressed; cells 12-ovuled (mature fruit unknown). — Arizona, locality not given (*Palmer*, 1869). Like the last abnormal in its obcompressed pod, and perhaps to be transferred, when better known, to *Physaria*.

DRABA \* SUBSESSILIS. Perennial, dwarf, densely cespitose, the

<sup>\*</sup> The North American species of Draba, exclusive of the Mexican, are the following:—

<sup>§ 1.</sup> EROPHILA, Lindbl. Petals bifid. — A stellate-pubescent scapose winterannual, with coarsely toothed or entire leaves, white flowers and many-seeded round-oval to oblong pods. *Erophila*, DC.

<sup>1.</sup> D. VERNA, Linn. — E. vulgaris, Americana, etc., DC. Naturalized from the Atlantic to Minnesota and Missouri, and at Vancouver, W. T. Identical with European forms.

numerous short branches of the caudex forming a broad mat, scapose, finely stellate-pubescent: leaves very small, oblong, obtuse, not ciliate:

- § 2. Heterodraba. Pedicels reflexed to one side. Seeds hispidulous. A stellate-pubescent short-caulescent and branching winter-annual, with coarsely toothed or entire leaves, white flowers and round-oval 8-12-seeded pods. *Heterodraba*, Greene, Bull. Calif. Acad. 1. 72.
- 2. D. UNILATERALIS, Jones. Branches elongated, lax: leaves cuneate-obovate to oblanceolate: racemes usually nearly sessile: flowers very small: pods somewhat twisted, on short pedicels. Torr. Bull. 9. 124. Colusa County, California, to Lower California.
- § 3. Drabella, DC. Stellate-pubescent or more or less villous short-caulescent and more or less leafy winter-annuals (scapose and rarely biennial in n. 12), with ascending or spreading pedicels, entire or emarginate petals and smooth seeds.
  - \* Early spring species of valleys and hillsides, or southern.
  - + Leaves entire: flowers small, white: pedicels clustered or approximate.
- 3. D. CAROLINIANA, Walt. Branches often decumbent, the peduncles scapelike: leaves loosely stellate-pubescent: pods linear, glabrous. — New England to Minnesota, Arkansas and Georgia; Umatilla, Oregon.

Var. MICRANTHA, Gray. Pods subappressed-hispid. — Illinois to Texas, New Mexico and Washington Territory.

- ← Leaves coarsely few-toothed or entire: pedicels more remotely racemose.
   ← Flowers small, white: stigma sessile or nearly so.
- 4. D. CUNEIFOLIA, Nutt. Loosely stellate-pubescent: leaves cuneate-obovate to oblanceolate: raceme pedunculate: pods linear-oblong, usually acutish, shortly subappressed-hispid, 16-50-seeded. D. filicautis, Scheele, Linnæa, 21. 588. Kentucky to Alabama and west to southern California.

Var. INTEGRIFOLIA. Small (1 or 2 inches high) with small and mostly entire leaves, and glabrous pods on pedicels about a line long. — Coast Ranges of southern California.

Var. PLATYCARPA. Pods oblong-oval, usually obtuse. — D. platycarpa, Torr. & Gray, Fl. 1. 108. D. Ræmeriana, Scheele, l. c. Texas to Arizona. Differing only in the form of the pods.

- 5. D. Sonoræ, Greene. Racemes usually nearly sessile and flowers very small: pods finely stellate-pubescent, narrowly oblong, 16-20-seeded, on short pedicels.—Bull. Calif. Acad. 2. 59. Southern California and Arizona to Sonora. The pubescence of the pods is the most constant character distinguishing this species from the last.
- 6. D. BRACHYCARPA, Nutt. Stellate pubescence somewhat appressed: leaves ovate to ovate-oblong, the cauline oblong-lanceolate or linear: peduncles short: flowers very small: pods narrowly oblong, glabrous, 1 or 2 lines long, 10-12-seeded. Virginia to Georgia, Louisiana and Missouri; Roseberg, Oregon.
  - ↔ ↔ Flowers yellow, large: style slender.
- 7. D. MOGOLLONICA, Greene. A span high, villous or loosely stellate-pubescent below: leaves mostly basal, oblanceolate, stellate-pubescent: pods linear or oblong, glabrous, 4 to 8 lines long. Coult. Bot. Gaz. 6. 157. Mountains of New Mexico (Rusby, Greene).



peduncles very short; fruiting raceme about an inch long and with the pod sparsely pubescent: flowers small, white, the petals scarcely longer

- 8. D. (?) ASPRELLA, Greene. Pubescent with spreading simple or forked hairs; scape-like peduncles one to several: filaments dilated downward: pods oblong-elliptical, somewhat turgid, hispid, on divaricate pedicels; style slender.

   Torr. Bull. 9. 125. Arizona. A doubtful species by reason of the turgid pod and dilated filaments. Mature fruit has not been seen.
- \* High mountain or northern species: leaves entire or few-toothed: flowers small, yellow, becoming whitish: stigma sessile.
- 9. D. NEMOROSA, Linn. Usually branching below, loosely stellate-pubescent: leaves rarely rosulate, ovate to oblong-lanceolate: racemes nearly sessile: pods narrowly oblong, or oblong-elliptical, acutish, minutely pubescent (rarely glabrous, var. leiocarpa, Lindbl.), 3 or 4 lines long; pedicels spreading or divaricate, 6 to 12 lines long. From the Great Lakes across the continent to Oregon, and northward. Europe and Siberia.
- 10. D. STENOLOBA, Ledeb. Simple or branching below, villous toward the base: leaves mostly subrosulate, oblong-obovate or oblanceolate, the 1 or 2 cauline ovate to oblong-lanceolate, mostly entire, usually more or less villous and ciliate: pods linear, acute, glabrous, 4 to 7 lines long, equalling or exceeding the spreading pedicels.—Subalpine, from Colorado to the Sierra Nevada and northward; Unalaska.
- 11. D. MONTANA, Watson. Stellate-pubescent throughout and somewhat villous, leafy: racemes nearly sessile: pods linear-oblong, finely pubescent, obtuse or acutish, longer than the erect or ascending pedicels. Proc. Am. Acad. 14. 289. Northern Colorado.
- 12. D. CRASSIFOLIA, Graham. Annual or biennial (?), very slender, glabrous throughout or the leaves ciliate: leaves in a basal tuft, narrowly oblanceolate: peduncles scape-like: pods lanceolate or oblong-lanceolate, acute, equalling or exceeding the spreading pedicels. Colorado and northward, and in the Sierra Nevada; Greenland.
- § 4. Drabea, Lindl. Perennial caulescent or scapose above the branching leafy-tufted caudex (sometimes biennial and simple-stemmed in species of • • ): leaves flat, soft, more or less broad, not carinate.
  - · Scapose.
  - + Flowers yellow: leaves entire (less than 6 lines long).
- 13. D. ALPINA, Linn. Caudex much branched, densely cespitose: leaves oblong-oblanceolate, with thick midvein at base, glabrous and villous-ciliate or somewhat villous-pubescent with simple or stellate hairs: scape pubescent: calyx villous: pods usually glabrous, ovate to oblong-ovate, acute; style short; stigma broad. D. pauciflora, R. Br. D. micropetala, Hook. Greenland; Arctic coast and islands; Hudson's Bay; Rocky Mountains (Drummond; D. rupestris, \$\beta\$, Hook. Fl. Bor.-Am.). Northern Europe; Siberia.
- 14. D. Howelli, Watson. Cespitose, finely stellate-pubescent throughout: leaves broadly spatulate: flowers large, deep yellow: pods pubescent, somewhat obliquely oblong, acute at each end, on spreading pedicels; style slender.—Proc. Am. Acad. 20. 854. Siskiyou Mountains, California (Howell).

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than the yellowish ovate sepals: pods broadly ovate-elliptical, acutish or obtuse, 2 lines long, ascending on pedicels about a line long; style

# + + Flowers white: leaves (mostly very small) entire or rarely few-toothed: scapes rarely with a single leaf.

18. D. NIVALIS, Liljeblad. Caudex with numerous slender matted branches: leaves oblanceolate, acutish, entire, with a stoutish midnerve, canescent with short dense stellate pubescence, ciliate near the base if at all: scapes and calyx pubescent: pods few on short pedicels, usually glabrous, oblong, acute at each end; style short, stout; stigma 2-lobed. — D. muricella, Wahl. D. stellata, var. nivalis, Regel. From Greenland and the Arctic coast to Labrador, Colorado, northern Utah and Nevada, and British Columbia. Iceland, Spitzbergen, and northern Europe. Flowers sometimes slightly tinged with yellow.

Var. ELONGATA. Leaves obtuse or acutish: scapes very slender: pods long (4 to 8 lines) and narrow, on rather longer pedicels. — D. lævipes, Hook. ? Rocky Mountains, from British America to Wyoming and the Uintas; Mt. Adams.

19. D. SUBSESSILIS, Watson. See page 255.

20. D. FLADNIZENSIS, Wulf. Leaves more loosely rosulate, narrowly oblanceolate, usually acute, entire, pilose-ciliate, usually sparsely villous or somewhat stellate-pubescent, rarely wholly glabrous: scapes usually glabrous; racemes short: petals often yellowish: pods glabrous, ovate-oblong or ovate, on short pedicels; stigma nearly sessile. — D. androsacea and D. Lapponica, Willd. D. lactea, Adams. D. Wahlenbergii, Hartm. Greenland to the lower St. Lawrence, and in the Rocky Mountains to Colorado. Europe and Asia.

Var. CORTMBOSA. Leaves occasionally toothed, ciliate and subpubescent: scapes and sepals usually pubescent: pods stellate-pubescent; style very short.

— D. corymbosa, R. Br. Greenland and perhaps (the original specimens) the west coast of Baffin's Bay. Many of the specimens from Greenland and those from Spitzbergen that have been placed here appear to belong, some to D. alpina and others to D. hirta.

<sup>15.</sup> D. LEMMONI, Watson. High alpine, densely cespitose: leaves thick, spatulate or oblong-obovate, ciliate and pilose with simple or forked hairs or nearly glabrous: scapes pilose: pods pubescent or glabrous, ovate to broadly lanceolate, somewhat twisted, on slender spreading pedicels; style short and stout.—Bot. Calif. 2. 430. D. alpina, var. algida, Bot. Calif. 1. 29, mainly. Peaks of the Sierra Nevada and of the Blue Mountains, Oregon.

<sup>16.</sup> D. VENTOSA, Gray. Cespitose, the slender branches of the caudex more or less densely leafy: leaves oblong-oblanceolate, densely stellate-pubescent or glabrate: pods ovate to oblong-lanceolate, densely pubescent to glabrous, on ascending pedicels; style short and slender.—Am. Nat. 8. 212. D. alpina, Watson, Bot. King, 20. Northern Utah and northwestern Wyoming; Stein's Mountain, southeastern Oregon.

<sup>17.</sup> D. EURYCARPA, Gray. Densely cespitose and stellate-pubescent: leaves oblanceolate, the scapes scarcely longer, few-flowered: pods large, oblong-obovate, acute, glabrous; style slender. — Proc. Am. Acad. 6. 520. Sierra Nevada (Brewer).

very short and thick. — On the White Mountains of Mono County, California, at 18,000 feet altitude (W. H. Shockley, July, 1886).

- \* Caulescent, the stems few- or many-leaved : leaves entire or few-toothed.
   Flowers vellow.
  - Lower leaves often an inch long or more.
- 21. D. HYPERBOREA, Desv. Pubescence of very short branching hairs: caudex stout, simple: leaves coarsely toothed, oblanceolate, or the cauline oblong-obovate: corymb broad: pods obtuse, broadly elliptical to narrowly oblong, usually glabrous, on spreading pedicels; style short.—Alaska, from Sitka to the Aleutian and St. Paul's Islands.
- 22. D. CHRYSANTHA, Watson. Caudex much branched; stems glabrous or loosely pubescent: leaves deep green, very narrowly oblanceolate to linear, rarely few-toothed, usually glabrous or sparingly ciliate: pods glabrous, oblong to oblong-lanceolate, on usually short pedicels; style short, slender. Proc. Am. Acad. 17. 364. High peaks of Colorado and Arizona.
- 23. D. STREPTOCARPA, Gray. Thinly villous with long simple or branched hairs; caudex simple or sparingly branched: leaves oblanceolate to (the cauline) oblong or lanceolate, rarely toothed, ciliate and villous: pods lanceolate, usually twisted, glabrous or pubescent on the margin, exceeding the ascending pedicels; style slender. Am. Journ. Sci. 2 ser. 83. 242. Mountains of Colorado and New Mexico; an Arizona form approaches the next.
- 24. D. AUREA, Vahl. Pubescent throughout with short stellate hairs, occasionally subpilose: leaves usually narrow, frequently ciliate at base: pods lanceolate to linear, acute, rarely glabrous; style short and stout, otherwise like the last. Greenland; Rocky Mountains, from British America to New Mexico and Arizona; Mignon Island, Gulf of St. Lawrence. A form with ovate pods occurs in Utah and Colorado.

Var. STYLOSA, Gray. Style very slender, a line long. — New Mexico (Fendler). A doubtful form from New Mexico and Arizona has broad ovate and entire cauline leaves.

- ↔ ↔ Leaves small, half an inch long or less.
- 25. D. AUREOLA, Watson. Rather densely stellate-pubescent throughout; caudex simple or branched; stem stout, simple: leaves numerous, oblanceolate, obtuse, entire, the cauline oblong: raceme short and dense; calyx glabrous: pods broadly oblong, obtuse, pubescent, flat, on short spreading pedicels; style short and stout. Bot. Calif. 2. 430. Lassen's Peak, California.
- 26. D. CORRUGATA, Watson, l. c. Pubescent throughout with loose branching hairs; stems branching from the base, very leafy: leaves entire, oblong-oblanceolate: calyx pubescent: pods lanceolate to broadly oblong, acute or obtuse, much corrugated and twisted; style long, attenuate to a minute stigma.

   San Bernardino Mountains, California.
  - + + Flowers white.
  - ↔ Stems simple or sparingly branched.
  - Cauline leaves usually several to many.
- 27. D. INCANA, Linn. Stellate-pubescent throughout, usually loosely; caudex often simple: leaves few-toothed or entire, oblanceolate or the cauline lanceo-

DRABA BREWERI. Dwarf and alpine, biennial or a short-lived perennial, the very shortly branched caudex sending up 2 to 6 or more simple leafy stems 1 to 3 inches high, canescent throughout with a fine dense stellate pubescence: basal leaves crowded, oblong

late to ovate: pods oblong to lanceolate, usually acute and flat, glabrous or finely pubescent, usually suberect on ascending pedicels; style very short.—

D. contorta and D. confusa, Ehrh. Greenland to Labrador, New Brunswick and northern Vermont, and in the Rocky Mountains to Colorado and British Columbia. Europe and Asia. Most western specimens are more finely and densely pubescent than is usual.

Var. ARABISANS. Caudex much branched: pod glabrous, acuminate or acute, often twisted; style longer. — D. arabisans, Michx. D. Canadensis, Brunet, a form with ovate pods. Labrador to northern Vermont and the shores of the Great Lakes. Grading indefinitely into the typical form.

- 28. D. Breweri, Watson. See above.
- 29. D. BOREALIS, DC. Loosely stellate-pubescent throughout, more or less cespitose: leaves ovate to oblong-ovate: pods broad, ovate to oblong ovate, flat, exceeding the pedicels; style short and stout.—D. Unalaschkiana, DC. D. incana, var. borealis, Torr. & Gray. Alaska and adjacent islands to British Columbia and the northern Arctic coast. Kamtchatka. A variety with longer pedicels (D. Sachalinensis, Schmidt) is found in Japan.
  - = = Cauline leaves usually one to three.
- 30. D. HIBTA, Linn. Loosely and often sparingly stellate-pubescent: caudex branched: leaves narrowly oblanceolate, or the cauline ovate, frequently more or less ciliate: pods oblong-lanceolate to -ovate, often twisted, glabrous or sparingly pubescent; style short and stout. D. oblongata and D. rupestris, R. Br. D. gracilis, Ledeb. Greenland to Alaska. Northern Europe and Asia.

Var. ARCTICA. Densely tusted and more densely pubescent: leaves short, the cauline ovate: pods pubescent.—D. arctica, Vahl. Greenland and Grinnell Land (Greeley). Spitzbergen.

- ↔ ↔ Stems diffusely branched above.
- 31. D. RAMOSISSIMA, Desv. Thinly stellate-pubescent, the caudex much branched: leaves oblanceolate, laciniately toothed: pods oval to narrowly oblong, pubescent, twisted; style long and slender. Mountains of Virginia and Tennessee; cliffs of Kentucky River.
- § 5. AIZOPSIS, DC. Scapose cespitose perennials: leaves linear, entire, becoming more or less rigid, carinate: flowers yellow.
- 82. D. GLACIALIS, Adams. Alpine or subalpine: leaves linear or linear-oblanceolate, more or less loosely (or densely) stellate-pubescent, sometimes ciliate at base: pods ovate to ovate-oblong, acute (rarely narrowly oblong and acute at both ends), usually finely pubescent; style short. D. oligosperma, Hook. D. alpina, var. glacialis, Dickie. From the arctic regions to Colorado, Utah, and California. Siberia and Spitzbergen. Quite variable.

Var. PECTINATA. Alpine and very densely cespitose, the short rigid leaves glabrous or nearly so and ciliate with long rigid hairs. — D. densifolia, Nutt. From northern Utah to the Sierra Nevada.

to linear-oblong, obtuse, entire or rarely sparingly toothed, 2 to 4 lines long, sometimes slightly ciliate at base, the cauline few (2 to 4), oblong-ovate: flowers small, white, the sepals oblong, herbaceous: pods linear-oblong, 2 or 3 lines long, obtusish, pubescent, ascending on short pedicels; stigma sessile or nearly so. — On Mt. Dana, at 12,000 feet altitude (W. H. Brewer, 1863); White Mountains, Mono County, at 13,000 feet (W. H. Shockley, July, 1886).

CHEIRANTHUS OCCIDENTALIS. Annual, low (6 inches high or less), erect, simple or branching from the base: leaves linear- or narrowly oblanceolate: flowers lemon or orange-color, 6 lines long: pods 2 to  $3\frac{1}{2}$  inches long by  $1\frac{1}{2}$  lines broad, beaked by a style 2 lines long, ascending on pedicels about 3 lines long: seeds narrowly winged. — Erysimum asperum, var. (?) pumilum, Watson, Bot. King's Expl. 24. In Washington Territory (Wallawalla, Lyall; Klickitat County, Suksdorf), Oregon (Wasco County, Suksdorf), and northern Nevada (near Carson City, Watson). Resembling dwarf states of Erysimum pumilum, to which it has been referred in the want of fruiting specimens, which are first collected by Mr. W. C. Suksdorf.

CAULANTHUS LEMMONI. A stout branching annual, 1 or 2 feet high, glaucous and glabrous or sparingly hispid with spreading simple or branched hairs: cauline leaves broadly auriculate-clasping, lanceolate, acuminate, entire, or the lower somewhat oblanceolate and toothed: racemes open, elongated, the streptanthoid flowers (sepals more or less brownish purple) spreading or reflexed on usually hispid pedicels: petals undulate, 6 or 8 lines long, the blade not broader than the claw, white veined with brown: pods subterete with nerved valves,  $2\frac{1}{2}$  to 5 inches long by  $1\frac{1}{2}$  lines broad, ascending; style very variable in length; stigmas divaricate. — Near Cholame, northeastern part of San Luis Obispo County, Calif. (J. G. and S. A. Lemmon, June, 1887).

SILENE LUISANA. Perennial, glandular-pubescent throughout, a foot high: leaves very narrowly linear, 2 inches long or less: peduncles 1-2-flowered, equalling the floral leaves: calyx narrowly cylindrical, 6 or 7 lines long, the teeth oblong-ovate, membranously margined and ciliate; petals white (?), 9 lines long, the oblong blade bifid to the middle, with or without small lateral teeth, the claw narrowly auriculate, and the narrowly oblong appendages acute and more or less lacerately toothed; filaments naked: capsule subcylindric, upon a stipe 1½ lines long, the small flattened seeds tuberculate, scarcely crested. — Nearest to S. verecunda. On rocks near San Luis Obispo (J. G. and S. A. Lemmon, n. 4557, June, 1887); also near Tolon, in Monterey County (T. S. Brandegee, 1886).

CALANDRINIA HOWELLII. Closely resembling C. Cotyledon: leaves more narrowly spatulate, 3 inches long or less, entire at the summit, the narrowly scarious margin crisped-undulate: scapes and inflorescence as in C. Cotyledon, but the flowers sessile or nearly so; petals 6 to 8; stamens 5 to 7, the narrow filaments slightly coherent below: ovary 2-4-valved; seeds 4 to 10.—On the Deer Creek Mountains in Josephine County, Oregon (Thomas Howell, July, 1887); also in cultivation at Cambridge. The leaves of C. Cotyledon are not at all crisped upon the margin, and have usually a few small teeth at the summit. The seeds of both species are ecarunculate, black and shining.

SIDALCEA HENDERSONI. Tall and apparently perennial (3 or 4 feet high), glabrous throughout, the stem simple or nearly so: leaves palmately 7-cleft to below the middle, the mostly broad segments coarsely lobed and toothed, the upper leaves 3-5-parted and the segments narrower: flowers large (9 to 12 lines long), in a loose raceme, the pedicels (1 to 3 lines long), shorter than the linear bracts: calyx large (\frac{1}{2}\) inch long in fruit), the lobes ovate-lanceolate, shortly acuminate: carpels few (8), smooth and glabrous, 2 lines long including the conspicuous linear beak. — Near the shore of Clatsop Bay, Oregon (L. F. Henderson, July, 1887).

TRIFOLIUM HOWELLII. Perennial (?), glabrous throughout, the stout stems 2 feet long: stipules large, lanceolate to ovate; petioles short; leaflets mostly cuneate-oblanceolate, 1\frac{1}{2} to 3 lines long, irregularly toothed: peduncles axillary, exceeding the leaves: heads naked, ovate or oblong, the short-pedicellate flowers soon reflexed: calyx-teeth narrow, about equalling the tube; corolla 4 or 5 lines long: pod 2-ovuled, 1-seeded, a little exceeding the calyx. — Of the T. ciliatum group. In the Siskiyou Mountains, southern Oregon (Thomas Howell, July, 1887).

ASTRAGALUS SYLVATICUS. Near A. tricarinatus and A. albens: glabrous, the decumbent or ascending stems a foot long or more: leaflets 8 to 10 pairs, oblong, retuse, 4 to 9 lines long: peduncles equalling or exceeding the leaves; racemes small, close (about an inch long): calyx very slightly pubescent, the acuminate teeth about equalling the campanulate tube; petals ochroleucous, 3 or 4 lines long: pod chartaceous, sessile, linear and more or less curved, compressed, 2-celled by the intrusion of the dorsal suture, the ventral acute, 6 to 8 lines long by 1½ broad. — Near Glendale in southern Oregon, "in open gravelly ground" (L. F. Henderson) or "in dense forests" (Thomas Howell, June, 1887, — who suggests the name).

ASTRAGALUS OXYPHYSUS, Gray. This species is described as having inflated pods. Fruiting specimens have recently been collected by Mr. Lemmon in the northern part of San Luis Obispo County, in which the pods are much compressed and distended only partially in the middle, both sutures being acute and the ventral one straight. The stipe is villous and as much exserted from the narrow calyx-tube as in A. leucopsis, which the species much resembles in appearance.

LATHYRUS CINCTUS. Sparingly pubescent throughout: stem stout, angled: stipules foliaceous, semihastate, lanceolate, nearly an inch long, the broad basal lobe coarsely toothed; leaflets 10 to 15 pairs, narrowly oblong, obtuse, mucronate, 1 to 1½ inches long: peduncles much shorter than the leaves, few-flowered: calyx short, the longer teeth equalling the tube; petals 6 lines long or more: pod nearly straight, broad, 1½ inches long by 5 or 6 inches wide, 3-5-seeded: seeds orbicular, nearly surrounded by the hilum, 2½ lines broad. — Near Tolon, Monterey County, California (T. S. Brandegee, 1886). A very distinctly marked species; turning black in drying.

LATHYRUS PALUSTRIS, Linn., var. (?) GRAMINIPOLIUS. Leaves very narrow and elongated, 2 to 4 inches long and often only a line wide or less; flowers variable in size and color, often yellow. — Frequent from New Mexico to Arizona and northern Mexico.

IVESIA SHOCKLEYI. Alpine, dwarf and cespitose, the stout muchbranched caudex compacted with the persistent remains of dead leaves, finely pubescent throughout and more or less glandular: leaves 1 to 1½ inches long or less, the petiole usually ciliate and somewhat villous at base; leaflets 3-parted, approximate or imbricated, rarely a line long, often setosely tipped: inflorescence open, few-flowered: calyx small, campanulate, becoming rotate, the deltoid lobes exceeding the white spatulate petals: stamens 5 or sometimes 10: pistils few (6 or less) upon a villous receptacle. — Summit of Silver Peak, Alpine County, California (J. G. Lemmon, 1873); in the White Mountains, Mono County, at 13,000 feet altitude (W. H. Shockley, 1886).

Pyrus (Sorbus) occidentalis. A shrub, 2 feet (Suksdorf) to 4 or 6 feet high (Brewer), glabrous or very nearly so: leaflets 3 or 4 (very rarely 5) pairs, oblong-elliptical, obtuse, sometimes mucronate, dentate usually only toward the apex (rarely below the middle) or sometimes entire, 1 to 2 inches long, the rhachis 3 or 4 inches long: cyme small and usually rather few-flowered: calyx glabrous: fruit pyriform, red, 4 lines long: seeds semicircular in outline, 1½ lines long.—In the mountains from Washington Territory to California (Cascade Mountains, Lyall; Mt. Adams, at 5-6,000 feet altitude, Suksdorf;

"Oregon," 148 Hall; at Summit in the Sierra Nevada, Bolander; on the Big Tree road at 6,000 feet altitude, 1960 Brewer, and in Ebbett's Pass at 6,500 to 8,500 feet, 2091 Brewer). The Californian specimens have the leaves more toothed and the cymes larger than the more northern ones. It is said by Mr. Suksdorf to grow at a higher altitude than P. sambucifolia, the fruit differing in shape and darker colored. The seeds are shorter and proportionally broader than those of P. sambucifolia. It appears to be the only form that has been collected in California.

SAXIFRAGA OCCIDENTALIS. Resembling S. Virginiensis; leaves often more or less densely rufous-tomentose beneath: inflorescence open, glabrous or somewhat glandular-pubescent: calyx free from the pistils, cleft nearly or quite to the base, the segments very obtuse, not reflexed; petals white, oblong-obovate, obtuse; filaments slender: seeds with a loose smooth testa. - From the Rocky Mountains of British America (Drummond) to British Columbia and Vancouver Island (Lyall, Macoun), Oregon (Cusick, Henderson, Howell), and the northern Sierra Nevada (Chico, Mrs. J. Bidwell, Gray). In S. Virginiensis the base of the calyx is somewhat broader and the segments acutish, the filaments are somewhat dilated at base, and the seeds are muricate-costate. Though it varies in pubescence the leaves appear to be never densely tomentose beneath, and it is probably not found far west of the Mississippi. S. eriophora of Arizona has seeds similar to those of S. occidentalis and is a close ally, but it differs in the campanulate short-lobed calyx which is adnate to the ovary. The seeds of S. reflexa are somewhat tuberculate-costate. The specific name is given to the species as the western correlative of the common eastern S. Virginiensis.

HARTWRIGHTIA, Gray. A new genus of Eupatoriaceæ, of the subtribe Piquerieæ. Heads few-flowered. Involucre turbinate-campanulate, of few narrow and nearly equal herbaceous bracts, somewhat in two rows, the inner more chaffy. Receptacle convex, with a few bracts near the margin resembling the inner involucral ones. Corolla regular, the very short tube and broadly funnelform throat little longer than the obtuse lobes of the limb. Anthers exappendiculate, obtuse, truncate at base. Style-branches long-exserted, linear, slightly thickened above. Achenes obpyramidal, acutely 5-angled, contracted at the summit, where the margin is callously lobed by a thickening of the angles. Pappus none.—A perennial erect herb, with alternate petiolate entire leaves, and loose paniculate corymbs of small heads. Flowers purplish.

H. FLORIDANA, Gray. Glabrous, but resinous-atomiferous throughout even to the corolla and achenes, 2 to 4 feet high, slender, branching above: leaves distant, narrowly oblong-oblanceolate or the upper linear, attenuate to a long petiole, obtuse or acutish, on the branches much reduced and linear or spatulate: heads few, 7-10-flowered, 2 lines long; involucral bracts 8 or 10, obtuse: achenes smooth, equalling the involucre. - In sphagnous swamps, Volusia County, Florida; discovered by Dr. S. Hart Wright, of Penn Yan, New York, in November, 1886, by whom it was sent to Dr. Gray. It was recognized as a new genus, but description and publication were delayed until more material could be examined. This was received only during Dr. Gray's last illness, and at Dr. Wright's request the genus is now pub-Dr. Gray left no notes upon its characters, but it is evidently closely allied to Gymnocoronis and Adenostemma, from which it is distinguished by habit, the alternate entire leaves, the narrower styles, the smooth thin-angled achenes, and the few bracts upon the receptacle embracing the outer ones. It is the only member of the Piqueriea that has been detected within our limits.

CHAPTALIA SEEMANNII, Benth. & Hook. Closely resembling C. nutans in appearance, from which it is distinguished by a number of short appressed distant bracts upon the scape, the "heads never nodding," and the short stout beaks of the achenes. This species has been found during the past season by Mr. Pringle in Chihuahua, and proves to be the same as specimens collected in New Mexico (Greene) and Arizona (2789 Lemmon), which are referred in the Synoptical Flora to C. nutans.

Pentstemon Shockley. Somewhat woody at base and branching, the branches erect,  $1\frac{1}{2}$  feet high, finely puberulent throughout: leaves nearly uniform in size, oblong-ovate, obtuse or acute, sessile or nearly so, undulate, entire, 3 to 5 lines long, the floral gradually smaller: flowers mostly solitary and nearly sessile in the axils; calyx 8 lines long, the lobes lanceolate, acuminate; corolla purplish, 5 lines long, only slightly dilated above and the oblong obtuse lobes nearly equal; sterile filament beardless: capsule equalling or a little exceeding the calyx. — On Miller Mountain, Esmeralda County, Nevada, at 8,000 feet altitude (W. H. Shockley, 1886). Of the P. deustus group; strongly marked by its small undulate leaves, its strict subspicate inflorescence, and very small narrow flowers.

ERIOGONUM PENDULUM. Near E. lachnogynum, a tall perennial, woody and branching at base, densely white-tomentose throughout, the scattered oblong-oblanceolate obtuse leaves (1 to 2½ inches long) and

foliaceous bracts subglabrate above: the broad inflorescence several times di- or trichotomous upon naked peduncles; pedicels mostly elongated and naked; involucres at first nodding, campanulate (1½ to 2 lines long), the deltoid teeth erect: flowers very small, densely tomentose, slightly exserted. — Near Waldo, southern Oregon (T. Howell, July, 1887).

ERIOGONUM (§ VIRGATA) CITHARÆFORME. Annual, prostrate or procumbent, branching from the base, mostly glabrous excepting the floccose-woolly lower surface of the leaves; stems a foot high or less, several times 2-3-plurichotomous, the lower bracts foliaceous, the upper small and triangular: lower leaves 4 inches long or less, undulate, dilated and 3-5-nerved at the summit, the rounded blade abruptly contracted into the long winged petiole: involucres glabrous, broadly turbinate, with broad teeth, 1 to 1½ lines long; flowers rose-color, a line long, the segments spatulate-obovate. — Nearest to E. gracile. Found by J. G. Lemmon (n. 1584) on Baron Schroeder's ranch, 30 miles north of San Luis Obispo, in June, 1887.

TILLANDSIA (DIAPHORANTHEMA) WILSONI. Stem simple, very short (about  $\frac{1}{2}$  inch): leaves numerous, 1 to 3 or 4 inches long, gradually narrowed from the clasping base to the long-attenuate apex, channelled above, more or less hoary with minute appressed peltate brown-centred scales: peduncle very slender, recurved, about equalling the leaves, with 2 distinct bracts, probably 1-3-flowered: flowers and capsules not seen. — Abundant upon dead branches of the red cedar in a hummock skirting the Pithlachascotee River in Hernando County, Florida, about two miles above its mouth, where it was discovered, in 1887, by Dr. W. P. Wilson, of the University of Pennsylvania. It is in cultivation at Cambridge, but has not yet flowered; very distinct from all our other species.

BRODIEA HENDERSONI. Closely related to B. Bridgesii: scape and leaves about a foot high, the leaves 3 to 5 lines broad: pedicels about an inch long: corolla salmon-color with often broad brown-purple nerves, 6 to 12 lines long, the narrowly turbinate tube shorter than or barely equalling the limb: stamens in one row at the throat, the slender equal filaments scarcely or but slightly broader near the insertion, somewhat wing-dilated below within the tube; anthers very short: capsule ovate, shorter than the stipe. — Near Ashland, Jackson County, Oregon (L. F. Henderson, July, 1884 and 1886).

CALOCHORTUS (MARIPOSA) HOWELLII. Of the C. nitidus group; stem erect, a foot high or more, 1-2-flowered: leaves very narrow, the cauline (one and a floral pair) short; sepals ovate, shortly acumi-

nate; petals yellowish-white, an inch long, denticulate, slightly ciliate near the base, covered within with short crisped hairs, those above the gland denser and brown-purple; gland transversely oblong, densely covered with short yellow hairs: anthers oblong-lanceolate, acute and apiculate, 3 lines long: capsule elliptical, acute, 9 lines long. — Found near Waldo, Oregon, in 1884, and at Roseburg in 1887, by Thomas Howell.

Juncus Oreganus. Near J. supiniformis: stems numerous from very slender matted rootstocks, low (a span high or much less), very slender, exceeding the very narrow leaves, simply paniculate: heads few-flowered, often proliferous: sepals nearly equal, lanceolate, acute, twice longer than the six stamens; filaments about equalling the anthers: capsule dark brown, acutish, mucronate, at length nearly twice longer than the sepals (2½ lines long); seeds rather turgid, about 20-costate, with transverse lines between the costæ.— In bogs at Ilwasco, southern Oregon (L. F. Henderson, 1886). Differing from J. supiniformis in its comparatively shorter leaves, proliferous habit, hexandrous flowers, often larger capsules, and more turgid and more strongly marked seeds, which in J. supiniformis are narrowly oblong, and faintly 12-15-striate without cross-markings.

# 2. Some New Species of Mexican plants, chiefly of Mr. C. G. Pringle's collection in the mountains of Chihuahua, in 1887.

THALICTRUM GRANDIFOLIUM. Tall and glabrous or "sometimes pubescent:" leaves ample, 3-4-ternate, petiolate, with dilated stipules; leaflets very large (1 to  $2\frac{1}{2}$  inches long), somewhat obliquely rounded, often cordate (or the uppermost cuneate) at base, obtusely lobed, the prominent veins beneath with scattered short stout curved hairs: inflorescence diocious, open and spreading, somewhat leafy-bracteate; pedicels elongated, nodding at the summit: carpels  $2\frac{1}{2}$  lines long, semicircular, beaked by the short stout base of the very long (3 or 4 lines) filiform style, compressed, faintly and irregularly nerved: seed filling the cavity, flattened-subovate. — Collected by Mr. Pringle (n. 1513) under cliffs of the Sierra Madre, Chihuahua, Oct., 1887.

Thalictrum pinnatum. Glabrous and glaucous, slender, scarcely 2 feet high, from a fascicled tubero-fibrous root: leaves lanceolate in outline,  $2\frac{1}{2}$  inches long or less, very shortly petiolate and estipulate, pinnate with about 7 (or fewer) pairs of divisions, the lower divisions ternate with small lobed leaflets, the upper reduced to a single 3-lobed

leaflet: flowers diœcious; sepals of the fertile flowers very small: stigmas short and rather thick; achenes ovate, about a line long, undulately ribbed, the ovate seed filling the cavity.—On pine plains at the eastern base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1181), Sept., 1887.

THALICTRUM WRIGHTII, Gray. Mr. Pringle also collected in the Sierra Madre specimens of this species, which accord in every way with Wright's original specimens from Sonora. It appears to be clearly distinguishable from all forms of *T. Fendleri* by the very prominent reticulate venation of the leaflets.

DELPHINIUM VIRIDE. Glaucous; root rather thick, branching; stem about 2 feet high, glabrous: leaves pubescent, pedately cleft, with segments acutely lobed, the upper distant, more deeply divided and segments narrower: raceme few-flowered, the pedicels (1 or 2 inches long) glabrous or more or less reflexed-pubescent: calyx pubescent, yellowish green, the lanceolate sepals 6 lines, and the stout nearly straight spur about 10 lines long; petals purple, 3 lines long, the lateral with an oblong-lanceolate entire or cleft villous blade: capsules very finely pubescent: seeds large, marginately angled, with a close dark and somewhat rugose testa. — On gravelly bluffs of streams at the east base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1185), Sept., 1887. Peculiar in its green calyx and short purple petals.

HELIANTHEMUM PRINGLEI. Puberulent throughout; stems herbaceous, erect, a foot high, branching above: leaves oblanceolate, scabrous on the margin, an inch long by a line or two wide, the upper much reduced: inflorescence open, the slender pedicels jointed usually near the middle; flowers perfect; sepals 2 lines long or more, the outer shorter and linear, the inner ovate, acute, purplish; petals broadly flabelliform, entire, 4 lines long: stamens 20 to 25: capsule triangular-globose, a little shorter than the calyx. — On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1186), Sept., 1887.

HELIANTHEMUM CHIHUAHUENSE. Villous throughout; stems also finely pubescent, numerous, herbaceous or somewhat woody at base, 6 inches high: leaves oblong-oblanceolate, about 9 lines long by 2 broad, with much smaller ones fascicled in the axils: flowers in short few-flowered axillary and terminal corymbs, on short pedicels, jointed near the middle and bracteolate or at the base and naked, perfect, dimorphous, the lower apetalous and octandrous, the upper with emarginate petals (4 lines long) and 25 to 30 stamens; sepals

2 lines long, the outer linear, the inner ovate, acute: capsule nearly equalling the calyx.—In the same region; C. G. Pringle (n. 1187), Oct., 1887.

SILENE PRINGLEI. Finely roughish-tomentose and subglandular, slender, erect, 1 to 3 feet high: leaves linear-lanceolate, acuminate, narrowed to the base, 3 to 7 inches long: inflorescence more or less elongated, the peduncles at each node 1-3-flowered, erect, slender: calyx narrow, 10-nerved, 7 or 8 lines long, the ovate teeth fimbriate-ciliate; petals an inch long, dull brownish-purple (?), auricles prominent, appendages large and saccate, entire, the blade bifid to below the middle with a tooth on each side: stamens and styles scarcely exserted: capsule oblong-ovate, stipitate: seeds finely tuberculate.—On cool slopes at the base of cliffs in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1190), Oct., 1887.

CERASTIUM MADRENSE. Perennial (?), a foot high or more, viscid-pubescent throughout: leaves mostly radical, obloug- to narrowly oblanceolate, 2 inches long, glabrous above, sparsely villous beneath and villous-ciliate, the cauline few and distant, linear-lanceolate to linear: inflorescence cymosely paniculate, the flowers on slender pedicels an inch long, nodding in fruit; bracts small: fruiting calyx  $2\frac{1}{2}$  to  $3\frac{1}{2}$  lines long, the exserted capsule slightly curved. — On the cool summits of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1504), Oct., 1887.

MALVASTRUM JACENS, Watson. An erect form of this with more deeply lobed leaves was collected by Mr. Pringle (n. 1199) on sandy stream-banks in the Sierra Madre. This species is referred by Dr. Gray (Proc. Amer. Acad. 22. 288) to M. Peruvianum, from which it differs especially in its fascicled clusters of flowers in the axils or on short peduncles, not "at length evolute into unilateral spikes," and in the fewer (6, rarely 8) and more turgid carpels.

HIBISCUS SPIRALIS, Cav.? Collected by Mr. Pringle (n. 1452) in the valley of Mexico; differing from *H. tubiflorus*, DC., chiefly in the more shrubby habit, the small leaves more cuneate at base, and the shorter blunt lobes of the calyx.

LINUM PRINGLEI. Biennial (or sometimes perennial?), erect and rather strictly branched from the base, the stems with slender ascending branches above, glabrous and glaucous: leaves numerous, erect and more or less imbricated, without glandular stipules, oblong-oblanceolate, acute, 6 lines long or less: inflorescence loose; pedicels slender: sepals lanceolate, carinate, slightly scabrous on the margin, 1½ lines long; petals white, twice longer: capsule broadly ovate,

blunt, the erect styles somewhat coherent below; dissepiments ciliate. — On shaded slopes in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1200), Sept., 1887. Somewhat resembling *L. Greggii*, under which name it has been distributed.

CEANOTHUS AZUREUS, Desf., var. (?) PARVIFOLIUS. A widely branching shrub, with slender branchlets and small narrow leaves, 3 to 9 lines long; fascicles of flowers in a very short, mostly naked, racemelike thyrse (an inch long or less), the pedicels scarcely a line long.—On rocky slopes of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1205), Oct., 1887.

LUPINUS MONTANUS, H.B.K., var. GLABRIOR. A nearly glabrous form, with some fine pubescence.— On high wooded slopes of the Sierra Madre, Chihuahua, at 9,700 feet altitude; C. G. Pringle (n. 1206), Oct., 1887. There can be little doubt that this species includes both *L. vaginatus*, Cham. & Schlecht., and *L. flagillaris*, Bertol.

HOSACKIA CHIHUAHUANA. Annual, erect, very finely appressed-pubescent, a foot high; stipules foliaceous, small (about a line long), oblong-oblanceolate; leaves shortly petiolate, 5-7-foliolate, the leaflets oblanceolate, acute to retuse, 6 lines long or less: peduncles about equalling the leaves, 1-3-flowered, the bract at the summit small, trifoliolate; calyx 2 lines long, the teeth as long as the tube; petals yellow, turning brownish purple: pod nearly straight, about an inch long. — On shaded rocky slopes in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1210), Sept., 1887. Differing from H. gracilis in pubescence, small stipules, shorter petioles, and shorter calyx.

ASTRAGALUS YAQUIANUS. Of the *Mollissimi*; tomentose (the leaflets appressed-villous), perennial, the ascending stems a foot high: leaflets 10 to 15 pairs, narrowly oblong, acute or subacuminate, 6 to 12 lines long: peduncles stout, about equalling the leaves: flowers yellow, becoming reflexed, 8 to 10 lines long; calyx white-tomentose, half as long, the linear teeth shorter than the cylindrical tube; petals erect: ovary and pod glabrous, 2-celled, the latter erect, sessile, coriaceous, compressed-ovate, deeply sulcate on the back, ½ inch long.—On moist banks and gravelly bars of the upper Yaqui River at Guerrero, Chihuahua; C. G. Pringle (n. 1218), Sept., 1887.

ASTRAGALUS SCALARIS. § Scytocarpi; biennial, very sparingly and finely pubescent, the suberect very slender stems 2 feet high: leaflets 10 to 12 pairs, linear, 2 to 6 lines long, retuse or obtuse: peduncles equalling or exceeding the leaves, bearing a slender raceme of small distant spreading flowers: calyx campanulate, a line long, with short

acute teeth; petals purple,  $2\frac{1}{2}$  lines long, the banner spreading: pods reflexed, glabrous, sessile, 1-celled, thin-coriaceous, oblong or oblong-ovate, turgid, obtuse, nearly 3 lines long. — By streams in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1220), Sept., 1887. Somewhat resembling A. flexuosus, but with much shorter pods.

Brongniartia minutifolia, Watson, var. Canescens. Similar to Dr. Havard's original specimens from western Texas, but canescent with short appressed hairs and the stipules linear instead of oblong; a round bush, about 2 feet high. — Plains, at Orfiz, Chihuahua; C. G. Pringle (n. 1449), 1887.

Brongniartia sericea, Schlecht. Valley of Mexico; C. G. Pringle (n. 1454), 1887. Agreeing with Schlechtendal's description except in the fewer (2 or 3) peduncles and narrower bractlets.

Desmodium (Heteroloma) Pringlei. Erect, herbaceous, tall (4 or 5 feet), branching, the terete stem and branches and the long petioles rough with rather dense short stiff hooked hairs: stipules lanceolate, acuminate; leaflets thin, broadly ovate to ovate-elliptical, rounded or subcuneate at base, obtuse, 1½ to 3 inches long and nearly as broad, thinly strigillose-villous on both sides: fruiting racemes elongated; bracts ovate, acuminate; pedicels in pairs, widely spreading, 6 to 9 lines long: pods 4-7-jointed, the dorsal margin less deeply notched than the ventral, the joints 2 to 3 lines long, densely uncinate-pubescent. — In the shade on dry rocky ledges, Arroyo Aucho, in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1226), Oct., 1887. Near D. strobilaceum.

Desmodium (Heteroloma) Mexicanum. Perennial, herbaceous, trailing, the angled stems and branches (3 or 4 feet long) hispid with straight spreading and with shorter stiff hooked hairs: stipules lanceolate, acuminate, villous; petioles very short; leaflets orbicular to round-ovate, truncate or subcordate at base, thinly villous both sides and ciliate (substrigillose above), the larger 2 inches broad: racemes axillary and terminal, hooked-pubescent; pedicels distant, in pairs, spreading, about 6 lines long, the small bracts and broad calyx somewhat villous: pods 3-7-jointed, the sutures nearly equally indented; joints suborbicular, finely uncinate-pubescent, 2 lines long.—On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1227), Sept., 1887. Allied to D. molliculum.

COLOGANIA PRINGLEI. Perennial, with short procumbent slender stems, the pubescence reflexed and hispid: leaves nearly sessile; leaf-lets small (the larger 6 to 10 lines long), obovate, rounded or subretuse at the summit, glabrous above, sparingly appressed-hairy



beneath: flowers mostly sessile or nearly so and undeveloped, sometimes pedunculate and larger, the caly sparingly short-hairy: pods usually glabrous or slightly hairy on the sutures, sometimes thinly covered with short appressed hairs, 8 to 10 lines long, attenuate at base, 3-8-seeded. — On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1499), Oct., 1887. Resembling C. Martia, C. humifusa, and C. Lemmoni in habit and in its dimorphous sessile or pedunculate flowers.

LEUCENA GREGGII. A small tree, 10 to 15 feet high, the young parts finely pubescent with short spreading yellowish hairs, becoming glabrate: stipules triangular-ovate, acuminate; pinnæ 5 to 7 pairs, with a conspicuous subcylindrical gland at the base of each; leaflets numerous (15 to 30 pairs), narrowly oblong, acute or subacuminate, 3 to 6 lines long, the lateral nerves none or very faint: peduncles axillary, solitary or in pairs, 1 to 3 inches long: pods linear, 8 inches long by 4 to 6 lines broad, attenuate below to a short stout stipe and beaked with a slender style 1 or 2 inches long: seeds longitudinal.—

Near Rinconada (Dr. Gregg, 1847), at Saltillo (307 Palmer, 1880, distributed as L. glauca), and mountains near Monterey (C. S. Sargent, 1887). Distinguished from L. glauca by the glands of the rhachis, the more faintly nerved leaflets, the narrower thicker and long-attenuate pod, and the longitudinal seeds.

PITHECOLOBIUM PALMERI, Hemsl., var. RECURVUM. Flowering specimens which closely resemble this species, but have the rather short spines strongly recurved, were found in the Mapula Mountains, Chihuahua, by C. G. Pringle, April, 1887.

Potentilla Pringlei. Stems decumbent, a foot long or more including the paniculate few-flowered inflorescence, finely tomentose: leaves mostly radical, ternately digitate; leaflets broadly linear (1 or 2 inches long by about 2 lines broad), acutely toothed, nearly glabrous above, densely white-tomentose beneath: flowers on very slender pedicels, rather large, yellow; calyx-lobes lanceolate, the accessory lobes linear: stamens 20: styles filiform, nearly terminal. — On pine plains near the Sierra Madre, Chihuahua; C. G. Pringle (n. 1494), Sept., 1887. Near P. gracilis.

TILLEA VIRIDIS. Stems numerous, much branched, spreading, about 2 inches long: leaves narrowly linear, acute: flowers solitary in the axils, very shortly pedicellate, minute; sepals broad and rounded; petals twice longer, equalling the carpels, obtuse: follicles green, obtuse, 8-seeded, less than half a line long.—Wet places, base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1561), Oct., 1887.

SEDUM PRINGLEI. Annual, glabrous; stems 2 or 3 inches high, from a slender subtuberous root, leafy, several times dichotomously forked above: leaves sessile, oblong-lanceolate, obtuse, 3 lines long: flowers few upon the branches, very shortly pedicellate: sepals about a line long, the lanceolate acutish pale-rose petals twice longer: filaments subulate, shorter than the petals; scales oblong-spatulate, firm and thick: carpels erect, acutish, the styles very short. — In thin soil on hillsides near Cusihuiriachic, Chihuahua; C. G. Pringle (n. 1239), Aug., 1887.

SEDUM CHIHUAHUENSE. Annual, glabrous; stems erect from a small oblong tuber, 3 to 5 inches high, repeatedly dichotomous above: leaves sessile, oblong or oblong-lanceolate, obtuse, 3 or 4 lines long: flowers sessile or very shortly pedicellate upon the slender branches; sepals broadly oblong, obtuse, 1 becoming 1½ lines long; petals white, oblanceolate, 2 lines long: stamens included; scales clavate, slender: carpels shorter than the petals, attenuate above, at length divergent.

— Nearly allied to the last and to S. fuscum, Hemsl. In thin soil on rocky ledges in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1240), Sept., 1887.

SEDUM MADRENSE. Perennial, with a somewhat creeping root-stock, the branching stems 6 inches high or less, leafy, glabrous: leaves numerous, sessile, ligulate-oblanceolate, obtusish, 3 or 4 lines long: flowers shortly pedicellate in loose spreading cymes: sepals oblong, obtuse, 2 lines long; petals purple, linear-lanceolate, obtuse, 3 to  $3\frac{1}{2}$  lines long: stamens included, the scales very short and truncate-flabelliform: carpels equalling the petals, acuminate with the slender styles, becoming divaricately divergent. — On dry ledges in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1241), Oct., 1887.

SEDUM PUBERULUM. Rough-puberulent throughout; stems from a dense cluster of fibrous and fleshy roots, slender, simple or once forked, 1 to 3 inches high: leaves sessile, oblong or the upper linear-oblong, acute or acutish, 3 to 5 lines long: flowers few, sessile or shortly pedicellate; sepals narrowly oblong, 2 or 3 lines long; petals white, oblanceolate, acute, 3 lines long, scarcely exceeding the stamens; scales short, quadrangular: carpels erect, acuminate with slender styles. — On shaded cliffs in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1242), Oct., 1887.

ROTALA MEXICANA, Cham. & Schlecht. The leaves all opposite and the calyx appendaged at the sinuses.—In wet places on the plains near Guerrero, Chihuahua; C. G. Pringle (n. 1365), Sept., 1887.

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EPILOBIUM MADRENSE. Glabrous throughout and very glaucous; stems ascending from very slender rooting rhizomes, a span high or less, slender and somewhat flexuous, simple, terete or nearly so: leaves thickish, opposite (the floral alternate), petiolate, entire or obsoletely toothed, narrowly lanceolate or oblong-lanceolate, acutish, 6 to 12 lines long: flowers long-pedicellate; petals purple, 2 lines long, the lobes of the calyx scarcely half as long: capsule 1 to  $1\frac{1}{2}$  inches long: seeds oblong, obtuse, papillose. — With the habit of the *E. origanifolium* group; apparently not referrible to any of Haussknecht's species. In the Sierra Madre, Chihuahua; C. G. Pringle (n. 1245), 1887.

Sicyos (Heterosicyos) minimus. Small and very slender (stems 2 feet long or less), glabrous or nearly so: tendrils simple; leaves thin, shortly petiolate, ternately digitate, the lateral leaflets lobed on the lower side, the middle one narrowly lanceolate to linear,  $1\frac{1}{2}$  inches long or less, entire or sparingly toothed: male and female flowers in the same axils, minute, the male inflorescence few-flowered and much shorter than the petioles, the female flowers solitary or in pairs: fruit small (3 lines long), membranous, compressed, strongly gibbous and subtriangular, the ventral side straight, shortly beaked, sparingly covered with very short curved bristles: seed inverted, pendulous upon a funicle as long as the seed, ovate, somewhat rugose-tuberculate. — In cañons of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1576), Oct., 1887. Very peculiar in its thin pericarp, inverted long-funicular seed, and simple tendrils, and deserving at least sectional rank in the genus.

ERYNGIUM MADRENSE. Erect, 2 feet high or more, branching above: lower leaves unknown; cauline bipinnatifid, 2 or 3 inches long, the rhachis and distant segments linear-subulate and spinulose; the uppermost subdigitately parted, the segments entire or toothed; involucral bracts about 8, linear-subulate, spinulose, entire or with 1 or 2 teeth, 4 to 8 lines long: head oblong (4 or 5 lines long by 2 or 3 broad), the axis prolonged and 2-5-cleft at top; floral bracts flattened-filiform, about equalling the flowers: fruit about  $\frac{1}{3}$  line long, ovate, crowned with the purple calyx and covered with white tubercles in about 12 rows.—In ponds on the plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1531), Oct., 1887.

Bowlesia Palmata, Ruiz & Pavon. Under cliffs in caffons of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1248), Oct., 1887. Apparently agreeing in every respect with the descriptions of this Peruvian species, and with specimens collected in the Andes by Mr. Ball. PRIONOSCIADIUM; new genus of Umbelliferæ, near Angelica. Calyx-teeth very short, but nearly equalling or exceeding the depressed stylopodium. Fruit round-ovate, dorsally compressed, with a broad commissure; lateral jugæ expanded into lateral wings, the intermediate and dorsal somewhat prominent or slightly winged; vittæ several in the intervals and on the commissure. Carpophore 2-parted. Seed dorsally compressed, the margins infolded. — Erect, caulescent, with ample twice or thrice pinnate or pinnatifid leaves and mostly lobed or decompound leaflets, and compound umbels with no involucres and small involucels. Distinguished from Angelica (Archangelica) chiefly by the infolded seed. The name has reference to the mountain habitat of Pringle's specimens (πρίων, a saw, sierra).

PRIONOSCIADIUM MADRENSE. Perennial (?), 2 or 3 feet high, much branched, glabrous excepting the somewhat scabrous petioles and inflorescence: petioles shortly dilated at base; lower leaves thrice pinnate, the uppermost simply pinnate; leaflets lanceolate in outline, pinnatifid with rather small incised segments: peduncles short; umbels 6-10-rayed, the rays about an inch long; involucels of a few linear acuminate bracts; pedicels 1 to 3 lines long: fruit glabrous,  $3\frac{1}{2}$  to 5 lines long by  $2\frac{1}{2}$  to  $3\frac{1}{2}$  broad, the wings nearly as broad as the seed; vittæ in the intervals 3, very narrow and irregular, on the commissure 6, broad and thick. — On ledges of a river cañon near Guerrero, Chihuahua; C. G. Pringle (n. 1251), Sept. and Oct., 1887.

PRIONOSCIADIUM MEXICANUM. Stout and tall, the foliage and inflorescence subpubescent: leaves ternate and compoundly pinnate or pinnatifid, the ultimate segments large, oblong or lanceolate, subcrenately toothed and mostly lobed: peduncles verticillately panicled; rays 12 to 20, an inch long or less; involucels of a few linear acuminate bracts; pedicels very short (a line long or less): fruit nearly orbicular (a little narrower above), retuse, cordate at base, glabrous, 4 to 6 lines long, the wings broader than the seed; vittæ broad and nearly confluent, 3 in the intervals, 6 on the commissure. — Angelica Mexicana, Vatke, Ind. Sem. h. Berol. 1876, App. 2? The above description is drawn from Bourgeau's specimens from the valley of Mexico (n. 316, in flower, and n. 571, in fruit). Vatke's species was founded on specimens collected by Hahn in the valley of Mexico (n. 13, in fruit) and by Ehrenberg (n. 186) at Mineral del Monte. His description applies so closely to Bourgeau's specimens that the identity can scarcely be doubted, though the fruit is said to be that of a true Angelica and to have the intervallecular vittæ solitary and somewhat obscure.

PRIONOSCIADIUM PRINGLEI. Resembling the last in habit and foliage, rather more pubescent and the segments of the leaves more acutely toothed: fruit somewhat pubescent, on pedicels 1 or 2 lines long, oblong-elliptical, 4 or 5 lines long by  $2\frac{1}{2}$  or 3 broad, narrower below and scarcely at all retuse or cordate, the wings mostly narrower than the seed: vittæ broad and thin, 3 in the intervals, 6 on the commissure. — In the shade of cliffs on the Mapula Mountains (n. 1137) and on shaded slopes of La Bufa Mountain above Cusihuiriachic, Chihuahua (n. 1249); C. G. Pringle, Oct., 1886, and Sept., 1887. Distributed as Angelica Mexicana.

EULOPHUS TENUIFOLIUS. Glabrous; stems ascending, surrounded at base by the fibrous remains of old petioles, mostly simple, a foot high or more: leaves mostly radical, long-petioled, thrice pinnate, the linear leaflets very narrow, 2 to 5 lines long; solitary cauline leaf small, on a short dilated petiole: rays usually 10, about an inch long; involucels of several laciniately cleft bracts, mostly adnate to the short pedicels: flowers yellow: fruit ovate, acutish, 2 lines long or more; ribs slightly prominent: carpophore bifid or entire; vittæ numerous: seeds strongly lunate and deeply channelled. — In cañons of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1518), Oct., 1887.

EULOPHUS TERNATUS. Glabrous and glaucous; stem erect, much branched: radical leaves biternate, the leaflets very narrowly linear, entire, 1½ or 2 inches long or more; cauline leaves mostly ternate or the upper simple: umbels long-pedunculate, or the lateral often sessile, few- (usually 5-) rayed, the terminal involucrate with 1 or 2 long linear bracts; involucels none: flowers yellow: fruit round-ovate, obtuse, 1½ lines long; ribs obsolete; carpophore 2-parted; vittæ very numerous: seed deeply and broadly channelled. — Pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1252), Sept., 1887.

STEVIA PRINGLEI. Perennial, the herbaceous stems a foot high, simple above the branching base, purplish, sparingly appressed-pubescent: leaves approximate, mostly alternate (the lower only opposite), sessile, glabrous, linear (or the lower on the main stem oblong to oblong-ovate), obtuse, entire, about an inch long: heads few, on slender peduncles in a loose corymb; involucre slightly puberulent, purplish, 3 or 4 lines long: corollas pale purple, 5 or 6 lines long: achene puberulent, the pappus exaristate, short and coroniform, the paleæ somewhat connate. — Apparently near to S. pilosa, Lag. Foothills of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1301), Sept., 1887.

APLOPAPPUS (STENOTUS) NIVEUS. Caudex much branched, the herbaceous leafy ascending or decumbent stems 6 inches long and equalling the naked peduncle, white floccose-woolly throughout: leaves spatulate, 1 or 2 inches long by 3 to 9 lines broad, obtuse: peduncle 1-flowered, somewhat glandular-scabrous above; heads 6 lines long; involucre glandular-scabrous, not tomentose, of narrow acuminate bracts in 3 or 4 unequal rows: rays about 20, deep orange: achenes white-silky. — Gravelly borders of streams in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1300), Sept., 1887.

Sanvitalia tenuis. Annual, erect, a span high or less, slender, branching, rather sparingly rough-pubescent: leaves linear,  $\frac{1}{4}$  to 1 inch long, sessile, entire: heads small, sessile, the turbinate-campanulate to hemispherical involucres 2 lines high, of 1 or 2 series of thin obovate obtuse nearly equal bracts; receptacle small, depressed-conical, the chaff thin and that of the disk conduplicate: ligules very short, cuneate-obovate, 3-toothed; disk-flowers yellow becoming brown: achenes nearly alike in ray and disk, with two very slender deciduous awns or none, those of the ray usually more or less granular, of the disk with a thinner membranous margin. — In the Sierra Madre, Chihuahua, at 7-8,000 feet altitude; C. G. Pringle (n. 1304), Sept., 1887.

SIEGESBECKIA ORIENTALIS, Linn. A variety of this widely distributed species with small heads and very obtusely angled oblong-obovate achenes. — At Arroyo Aucho in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1283), Oct., 1887.

SABAZIA GLABRA. Glabrous throughout, branching from the base upward, a span high, lax: leaves entire, linear-oblong, obtuse, attenuate to a short petiole, 1 to  $1\frac{1}{2}$  inches long: peduncles 1-flowered, exceeding the leaves; outer involucre of 12 to 15 equal thin-herbaceous bracts, the inner embracing the achenes of the ray: ligules conspicuous, 3 or 4 lines long, rather broadly linear, 2-3-toothed, yellow toward the base, white or pinkish above: receptacle convex, broad.—In shallow water on the pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1295), Sept., 1887. The concave inner bracts of the involucre would refer this species strictly to Jagaria, but in other respects it agrees better with Sabazia.

LEPACHYS (OBELISCARIA) MEXICANA. Rough with a short spreading pubescence and somewhat hirsute, 2 feet high: lower leaves lance-olate, attenuate to a long petiole, acuminate, subcrenately toothed, the cauline pinnatifid with a few short spreading segments: heads long-pedunculate, 1 to 1½ inches long: rays yellow, narrowly oblong-spatulate, 15 lines long: achenes epappose, with obtuse naked margins, and

somewhat ribbed on the face. — On cool slopes of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1305), Sept., 1887.

HELIANTHELLA MADRENSIS. Root thick and fleshy: stems sparingly pubescent or glabrate, nearly naked, 2 feet high, bearing 3 to 5 long-pedunculate flowers: leaves mostly radical, linear and long-petiolate, acute or acuminate, 4 to 10 inches long (cauline much shorter), entire, glabrous above, subscabrous beneath: heads rather small (5 or 6 lines high); involucre finely pubescent, the bracts strongly 3-7-nerved: ray-flowers 9 lines long: chaff thin and scarious: pappus of 2 short slender awns and numerous dissected squamulæ. — On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1302), September, 1887. Allied to H. Mexicana.

BIDENS INERMIS. Annual, slender, branching, 2 feet high, hirsutely scabrous throughout: leaves ternately divided, the divisions ternately or pinnately cleft into broadly linear segments, the terminal one elongated: peduncles slender; involucre hirsute, the outer bracts narrowly linear, obtuse, the inner linear, acuminate, twice longer: ray white faintly veined with purple, 5 lines long, neutral: achenes numerous, unequal, very slender, mostly long-attenuate and 6 lines long, scabrous above, awnless. — On rocky ledges in thin soil, Arroyo Aucho, in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1291), Oct., 1887. Nearly allied to B. tenuisecta, but the achenes awnless as in B. exaristata.

SCHKUHRIA (EUSCHKUHRIA) PRINGLEI. With the habit of the genus, the leaves pinnately 3-7-parted with narrowly linear divisions, the uppermost entire: bracts of the involucre obtuse, with scarious yellow tips: flowers yellow: achenes (9) narrow, nearly 2 lines long, slightly hairy on the angles; pappus of very short unequal blunt nerveless scales, the longer scarcely half the length of the glandular base of the corolla. — In moist places on the plains near Guerrero, Chihuahua; C. G. Pringle (n. 1292), Sept., 1887.

HYMENOTHRIX GLANDULOSA. Annual or biennial, pubescent with spreading gland-tipped hairs, 2 feet high or more: leaves twice or thrice pinnate, the segments linear, obtuse: heads cymose; involucral bracts yellowish and somewhat scarious-margined: rays none; corolla of the disk-flowers with a dilated deeply lobed limb: achenes rather broadly obpyramidal and prominently angled, somewhat pubescent and hairy on the angles; pappus-scales very short and blunt, unequal, nerveless, not half the length of the glandular-hispid corolla-tube. — By springs in the Sierra Madre, Chihuahua, at 9,000 feet altitude;

C. G. Pringle (n. 1293), Oct., 1887. In the character of the pappus this species approaches Bahia still more nearly than does H. Palmeri.

TAGETES PRINGLEI. Annual, erect and branching, 2 feet high or more, glabrous: leaves simple, linear, serrate, ciliate toward the base, 2 or 3 inches long: heads few in the open cymes; involucres somewhat turgid, contracted and punctate above, with 5 blunt or apiculate teeth: flowers included, the 2 yellow rays scarcely exceeding the involucre: achenes linear, scarcely scabrous on the angles; awns 2 or 3, equalling the corolla or one shorter, the 2 or 3 paleæ short and blunt.— In wet places on the pine plains at base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1297), Sept., 1887. Allied to T. lucida.

PECTIS AQUATICA. Growing in shallow water, the floating stems a foot long, sparingly leafy and branched at top, glabrous and sparingly punctate: leaves linear, entire, not setose, an inch long: heads few and sessile or nearly so; involucre 3 to 5 lines long, of 5 imbricate obtuse purple-tipped bracts: flowers (about 12) included or nearly so; rays none: achenes very slender, with long-attenuate base, 3 or 4 lines long; pappus of 10 or 12 unequal scabrous bristles, the longest shorter than the corolla. — On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1296), Sept., 1887. A true Pectis, but of peculiar habit and the leaves wanting the usual ciliate bristles.

ARTEMISIA DRACUNCULINA. Closely resembling A. Dracunculus and A. dracunculoides: stem and leaves more or less villous with soft spreading hairs: leaves linear, entire or the cauline 3-cleft, 1 to  $2\frac{1}{2}$  inches long: panicle very loose, the heads (mostly ascending) on filiform peduncles 2 to 4 lines long; involucre nearly glabrous: sterile flowers numerous, the styles long-exserted. — At the base of cliffs in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1309), Oct., 1887. The whole plant, and especially the roots, have a decided odor.

Senecio umbraculifera. Densely and closely white-tomentose throughout, perennial, the stems erect from a horizontal rootstock,  $1\frac{1}{2}$  feet high: basal leaves linear-oblanceolate or linear, acute or acutish, attenuate to a short petiole, entire, 8 to 7 inches long, the cauline scarcely shorter, few (3 or 4), linear-lanceolate, sessile: heads approximate in a close cymose panicle, rather small, radiate; involucre narrowly campanulate, the bracts (10) 3 or 4 lines long: rays 5 or 6: achenes canescent. — Summits of the Sierra Madre, Chihuahua, at 9,700 feet altitude; C. G. Pringle (n. 1316), Oct., 1887. Near S. fastigiatus.

Senecio Chihuahuensis. Perennial (?), the purplish leafy subpubescent stem 1½ feet high, branching at the top: leaves thin, somewhat white-tomentose when young, glabrescent, the basal oblanceolate and coarsely toothed, 2 inches long, the cauline 2 to 4 inches long, ovate to oblong in outline, nearly sessile, pinnately divided, the narrow lobes usually sparingly pinnatifid or in the smaller leaves entire: inflorescence cymose; involucre calyculate, nearly glabrous, cylindric-campanulate, 3 or 4 lines long; bracts 12, linear, tipped with brown: rays 6 or 8, 4 lines long: achenes canescent.—On ledges of the Sierra Madre, Chihuahua, at 9,700 feet altitude, under *Populus tremuloides*; C. G. Pringle (n. 1318), Oct., 1887. Most nearly related to some forms of S. Douglasii.

HETEROTOMA GIBBOSA. Low and very slender, branching from the base, glabrous: leaves mostly radical, oblong-ovate, attenuate to a short ciliate petiole, coarsely toothed, an inch long; cauline 1 or 2, ovate, sessile, dentate: flowers on long slender pedicels, small (4 lines long); calyx very oblique; corolla blue with a greenish throat, the tube more or less gibbous at base but not at all calcarate, the upper lobe of the limb rounded, the lateral broadly oblong. — Banks of brooks, Ortiz, Chihuahua; C. G. Pringle (n. 1478), May, 1887.

POLEMONIUM PAUCIFLORUM. Perennial, a foot high or less, branching and leafy, glandular-pubescent: leaflets 6 to 12 pairs, narrowly lanceolate, acute, 9 lines long or less: flowers solitary or very few at the ends of the branches, on pedicels an inch long or less; calyx 6 lines long, the linear teeth longer than the campanulate tube; corolla yellow tinged with red, 1½ inches long, funnelform, the rather broad tube but little dilated above, the lobes broad, acute, 4 lines long: filaments declined, inserted near the base of the tube, the dilated appendage at the base pilose-bearded: capsule ovate, few-seeded, little exceeding the calyx-tube. — On shaded ledges in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1558), Oct., 1887. A true Polemonium though peculiar in the form and color of the corolla.

IPOMEA LEPTOSIPHON. Glabrous; stems very slender, from a narrow constricted tuber, branching and twining, 2 or 3 feet long: leaves shortly petiolate, digitately divided, the divisions very narrowly linear, 2 inches long or less and not ½ line wide: peduncles 1-flowered, about equalling the petiole: sepals unequal, oblong-lanceolate, acutish, the outer somewhat muricate, 4 or 5 lines long; corolla white or pinkish, nearly 4 inches long, funnelform with a long narrow tube: capsule ovate-globose, nearly equalling the calyx.— In thin gravelly soil on the foothills of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1887),

Sept., 1887. Resembling the *I. muricata* group, but the stem is evidently twining.

IPOMEA MADRENSIS. Glabrous; stems from a small oblong tuber, short (a span long), erect or decumbent, simple or divided at base: leaves very shortly petiolate, narrowly oblong, acute or acutish, narrowed at base, entire or with a single linear lobe on each side, 2 inches long: peduncles 1-flowered, ½ inch long, scabrous, bibracteate in the middle and often geniculate; sepals ovate, acute or obtuse, more or less muricate, 3 or 4 lines long; corolla purple, 15 lines long, funnelform with a very broad tube, apiculate at the folds: capsule globose, a little shorter than the calyx. — On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1338), Sept., 1887. Allied to I. leptophylla.

BREWERIA ROTUNDIFOLIA. Stems procumbent, herbaceous, several from a rather thick perennial (?) root, a span long or less, thinly pubescent: leaves round-ovate, 5 to 8 lines long, very obtuse or retuse, very shortly petiolate, glabrous above, silky-villous beneath: pedicels sessile in the axils, 1 or 2 lines long, shorter than the narrowly oblong acute bracts: sepals narrowly oblong, acute, nearly 2 lines long, equalling the globose capsule; corolla pale blue, open, 5 lines broad: filaments glabrous: styles distinct and divided to the base. — In damp places on the pine plains at base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1341), Sept., 1887. Allied to B. ovalifolia.

Pentstemon Pringlei. Near P. Jamesii, finely pubescent throughout, glandular above, a foot high or less: leaves narrowly oblong to lanceolate, obtuse or acutish, approximate, 1 to 1½ inches long, the lowest attenuate at base: peduncles mostly short, 1-2-flowered: calyx herbaceous, the segments oblong to lanceolate, obtuse or acute, 2 or 3 lines long; corolla apparently reddish purple, an inch long, ampliate above: sterile filament naked; anthers short, not expanded, ciliate. — On hills near Santa Isabel, Chihuahua; C. G. Pringle (n. 1557), Aug., 1887. The anthers are those of the Speciosi group.

VERONICA (VERONICASTRUM) MEXICANA. Stem herbaceous from a perennial running rootstock, erect, branching, a foot high or more, finely pubescent: leaves sessile or the lower very shortly petiolate, oblong-lanceolate, acute, cuneate at base, acutely serrate, 1 to  $1\frac{1}{2}$  inches long, sparingly pubescent: racemes terminal, loose, the lower bracts foliaceous; pedicels slender, 3 or 4 lines long: calyx unequally 5-lobed, the lobes oblong, obtuse,  $1\frac{1}{2}$  lines long; corolla blue, rotate with a very short tube, 4-lobed, 4 lines long. — On cool damp bluffs of streams in the Sierra Madre, Chihuahua; C. G. Pringle

(n. 1349), Sept., 1887. A very peculiar species, with large bright blue flowers.

PRIVA ORIZABÆ. With the habit, foliage and pubescence of *P. hispida:* leaves more acutely dentate: flowers distinctly pedicelled, the pedicels mostly equalling the linear bracts: calyx finely puberulent, narrowly cylindrical, in fruit globose-didymous: fruit ascending; cocci 1-celled, 1-seeded. — About Orizaba, Mexico; 2950 and 3118 Bourgeau, and 598 Botteri in Herb. Gray. Clearly distinct from *P. hispida*, in which the leaves are crenately toothed, the subcampanulate calyx densely uncinate-hispid, and the fruit more or less reflexed upon the very short pedicels. This last species was collected in the valley of Mexico by Bourgeau (n. 359) and Schaffner (n. 425), and in Chihuahua by Mr. Pringle (n. 287 of his 1885 collection, distributed as *P. echinata*).

MICROSTYLIS PRINGLEI. Stem slender, over a foot high, from a round-tuberous base, 1-foliate: leaf narrowly oblong above the sheathing base, acute, 2 inches long: raceme elongated, loose; bracts green, triangular-subulate, equalling or shorter than the very slender pedicels (about a line long): flowers 1½ lines long, very narrow, greenish yellow; lateral sepals narrowly lanceolate and subfalcate, acuminate, contiguous behind the lip, the lower lanceolate with a broad base, reflexed against the ovary; petals nearly filiform, much shorter, coiled backward; lip triangular-hastate, obtusish, a line long, with a dull brownish line near each margin; basal auricles oblong: ovary minute, mostly reflexed on the ascending pedicel. — On shaded gravel banks in the Sierra Madre, Chihuahua; C. G. Pringle (n. 1369), Oct., 1887. Near M. ocreata.

MICROSTYLIS CRISPATA, Reich. f.? A rather stout species, a foot high, with 2 or 3 oblong very acute or acutish loosely sheathing leaves about 4 inches long: raceme elongated (4 to 7 inches long) with numerous crowded flowers; bracts deltoid, acute, nearly equalling the very short thick erect pedicels: flowers greenish yellow; sepals oblong-ovate, obtuse, the margins revolute, the upper narrower, over a line long; petals linear, as long; lip cordate and concave-saccate, the pinkish acute apex thickened and cucullate: ovary and capsule strongly crispate-angled, the latter three lines long. — In cool damp soil in the Sierra Madre; C. G. Pringle (n. 1371), Sept., 1887. M. crispata is referred by Mr. Ridley, in his recent revision of the genus, to M. myurus, and he must have examined Hartwey's specimen in Herb. Kew upon which the species was founded, though he does not mention it in his paper. Mr. Pringle's specimens are nevertheless so

named at a venture, simply because they do not agree with the descriptions of *M. myurus*, upon the double chance of their being identical with Hartweg's plant and its yet proving to be a good species.

HABENARIA SCHAFFNERI. Stem stout, 8 inches high, covered with imbricated ovate or ovate-lanceolate sheathing, acute or acuminate leaves 1 to  $1\frac{1}{2}$  inches long: bracts large, foliaceous, much exceeding the ovary; raceme short, few- (6-8-) flowered: flowers large, 5 or 6 lines long; lower sepals lanceolate, acutish, the upper broadly elliptical, obtuse, carinate; petals 2-parted, the lower segments very narrow, the upper oblong-falcate, contiguous or subcoherent to the sepal; lip 3-lobed above the base, 5 lines long, the middle lobe narrowly ligulate, the lateral narrowly linear; spur an inch long or more, dilated toward the end and very acuminate: oblong processes of the stigma and beaks of the anther  $1\frac{1}{2}$  lines long.—In the San Miguelito Mountains (5088 Schaffner, 1876) and near San Luis Potosi (860 Parry and Palmer, 1878); under pines in the Sierra Madre, Chihuahua (1375a Pringle, Sept., 1887).

CALOCHORTUS MADRENSIS. Bulb small, fibrous-coated; stem very slender, a span high or less, not bulbiferous: leaves narrowly linear, equalling or shorter than the stem: flowers small, erect, orange-yellow; sepals oblong, obtuse, apiculate, 6 lines long, naked and spotless; petals as long, cuneate-obovate, rounded above or barely acutish, entire or denticulate, with a band of orange-colored hairs above the base, the nectary ill-defined or obsolete: anthers a line long, obtuse: capsule linear, 1 to 13 inches long. — On pine plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1382), Sept., 1887.

ERIOCAULON PRINGLEI. Annual, very low and delicate: leaves filiform, terete or semiterete, nerveless, 9 lines long or less: scapes very sleuder, 1½ inches long or less, with loose pellucid nerveless sheaths: heads small (less than a line broad) and few-flowered, fuliginous, glabrous; bracts erect, obtuse, the inner narrow and acute: flowers trimerous. — On plains at the base of the Sierra Madre, Chihuahua; C. G. Pringle (n. 1533), Sept., 1887.

## 3. Descriptions of some Plants of Guatemala.

LOUTERIDIUM; new genus of Acanthaceæ, tribe Ruellieæ. Calyx herbaceous, the upper sepals distinct, the 3 lower united to the apex, these 3 divisions nearly equal, acute. Corolla-tube very short, ab-

ruptly expanded into the large exceedingly oblique gibbous-campanulate throat; limb convolute in the bud, subequally 5-lobed, the lobes short. Stamens 2, exserted, inserted upon the tube, membranously dilated and subpubescent below, each connate with a very short obtuse staminodium; anthers oblong, dorsifixed, glabrous, the cells parallel. Capsule sessile, subtetragonal and somewhat dorsally compressed; cells 6-8-seeded. Seeds orbicular, flat, borne by stout acute retinacula, alternating in 2 rows in each cell. — A tall pubescent shrub with ample ovate leaves. Flowers long-pedunculate in an erect nearly naked cyme. A strongly characterized genus, having the habit of some species of Ruellia, but with the lower sepals united into one, two exserted stamens, and the corolla very oblique and inflated. Named with reference to the form of the corolla.

LOUTERIDIUM DONNELL-SMITHII. Twelve to fifteen feet high, sometimes arborescent, the younger branches, foliage and inflorescence soft-pubescent: leaves petiolate, ovate, acute, subcordate at base, finely crenate, 6 to 10 inches long by 4 to 6 wide: cyme a foot long or more; peduncles 3 or 4 inches long, jointed below the middle; bracts and bractlets very small or deciduous: divisions of the calvx oblong-lanceolate, usually acute or acuminate, an inch becoming 11 inches long; corolla-tube broad, 4 lines long, the saccately inflated gibbous throat (color indeterminate) an inch deep and nearly 11 inches broad, the somewhat contracted orifice bordered by the narrow spreading or at length revolute limb: stamens and style long-exserted: capsule narrowly oblong, an inch long: seeds 2 lines broad. — Near Pansamala in the department of Alta Vera Paz, Guatemala, at 3,800 feet altitude; Türckheim (n. 856), May, 1887. Communicated by John Donnell Smith, Esq., of Baltimore, well known as a zealous botanist, who is making a careful study of Türckheim's collections from central Guatemala.

Heliconia Choconiana. Glabrous throughout; stems about 3 feet high, sheathed with numerous leaves, the blades of which are sessile upon the sheaths, linear-oblong (6 to 10 inches long by about 2 broad), acuminate, green and shining: inflorescence deflexed upon the very short peduncle, the rhachis flexuous; spathes (5 or 6) scarlet, lanceolate, acuminate, about 2 inches long, the lower one empty and usually leafy-tipped: flowers yellowish white, 2 inches long; lower sepal free, the lateral connate with the petals: sterile stamen ovate, abruptly acuminate. — In the Chocon forests at the foot of limestone hills, March, 1885; in flower at Cambridge, March, 1887.

PLEUROTHALLIS BLAISDELLII. Stem slender, about 2 inches long,

angled, hispid, sheathed with 4 to 7 obliquely truncate funnelform acute nerved bracts, the terminal one sheathing the base of the solitary leaf and of the nearly sessile raceme: leaf oblong, nearly sessile, 1 or 2 inches long, acute at base, 3-denticulate at the apex, dark green, purplish beneath, 5-nerved, the outer nerve marginal: raceme usually solitary, about 6-flowered, much shorter than the leaf; pedicels very short, equalling the sheathing bracts: sepals brown-purple, 2 lines long, somewhat spreading, fleshy, oblong, acutish, the lower united to the middle; petals nearly equalling the column, thin, ciliate, broadoblong, obtusish, brownish above; lip somewhat longer, ligulate, ciliate, dark brown, not crested: column yellowish, narrow below, broadly winged above, the wings and crest ciliate-lacerate. - Chocon forests; described from plants in flower at Cambridge, November, 1887. Named in memory of Mr. Frank E. Blaisdell, the energetic young manager of the plantation of the "Tropical Products Company" upon the Chocon, to whom I was much indebted for assistance during my visit there in 1885.

PLEUROTHALLIS CHOCONIANA. Of the Apodæ cæspitosæ group: stems numerous, very short (1 or 2 lines) and slender, bearing a peduncle from the joint below the single leaf: leaf deep green (somewhat cæsious), oblong-oblanceolate, attenuate to a slender petiole, acute or obtusish and minutely bidentate at the apex, thick-margined, smooth above, many-striate beneath, 1 to 1 inch long: peduncle filiform, 2 to 4 inches long, 4-6 flowered; bracts minute; pedicels 1 to 8 lines long: lower sepals united very nearly to the apex, oblonglanceolate, gibbous and subsaccate at base, yellowish, faintly 4-nerved, 3 or 4 lines long, the upper somewhat shorter, lanceolate, acuminate, yellowish with 3 brownish nerves; petals equalling the column, oblong, acutish, pale yellow with brown midnerve; lip somewhat longer, ligulate, entire, obtuse, channelled, yellowish with 2 or 3 brown nerves: column white, narrowly winged, 2-calloused at the articulation with the lip. - In the Chocon forests and at the ruins of Quirigua, March and April, 1885. Described from plants in bloom at Cambridge, July, 1887.

PLEUROTHALLIS BRIGHAMI. Of the same group; stems very slender and closely cespitose: leaves bright green and shining on both sides, not striate nor margined, oblanceolate, acute and bidentate at the apex, attenuate at base, 1 or 2 inches long: peduncle filiform, equalling the leaf, usually 1-flowered; bracts sheathing, acuminate, 2½ lines long; pedicel 4 lines long: lateral sepals united to above the middle, somewhat gibbous, oblong, shortly acuminate, carinate, 4 lines

long, brown at base, yellowish above with 3 strong brown nerves; upper sepal oblong, acute, yellowish with brown nerves; petals spatulate, acutish, yellowish with a brown midnerve, equalling the green and brownish column (a line long); lip narrowly ligulate, dark brown.—On trees in the Chocon forests; described from plants in flower at Cambridge, August, 1887.

PLEUROTHALLIS MINUTIFLORA. Of the same group; cespitose, the stems very short and slender: leaves rather narrowly elliptical, 3-toothed at the apex, attenuate to the slender more or less elongated petiole, bright green, faintly margined and faintly few-nerved, the blade about an inch long: peduncle very short and slender from below the base of the leaf, the 3-6-flowered raceme about equalling the petiole; bracts ovate, acute, sheathing; pedicels a line long: perianth pale yellow, spreading; sepals lanceolate, \( \frac{3}{2} \) line long, the lower united to below the middle, subfalcate, acuminate, nerveless, the upper acute, faintly 1-nerved; petals linear-lanceolate, acuminate, a little shorter; lip thick and fleshy, broadly ligulate, papillose, orange-colored: column broadly winged. — Chocon forests; described from plants in flower at Cambridge, August, 1887.

SCAPHYGLOTTIS LONGICAULIS. Stems densely clustered, terete and slender, scarcely enlarged above the short slender base, the joints (the lower 4 inches long) covered below by a close thin whitish sheath: leaves linear and grass-like, 2 to 4 inches long by 1 to 1½ lines wide: flowers solitary or few, on short slender pedicels, the narrow ovary 6 lines long: sepals connivent, purplish, channelled, 3 lines long, the lower linear-oblong, broadening upward and obliquely truncate with a short lateral acumination, strongly gibbous at base, the upper linear-oblanceolate; petals apparently wanting; lip equalling and resembling the upper sepal but dilated toward the summit and broadly 3-lobed, the lateral lobes very thin, pale and incurved: column narrowly margined, whitish, nearly equalling the sepals. — From the Chocon forests; in flower at Cambridge, November, 1887.

MAXILLABIA YZABALANA. Of the Acades section; pseudobulbs compressed-globose, smooth, 1 to 2 inches in diameter, bearing a single flat coriaceous leaf complicate at base into a petiole \(\frac{1}{2}\) to 1\(\frac{1}{2}\) inches long, the blade 4 to 10 inches long by \(\frac{1}{2}\) to 1\(\frac{1}{2}\) broad, acute: flower fragrant, subdeclinate, the pedicel and ovary covered by 3 or 4 ovate imbricated greenish bracts 9 lines long: perianth connivent, the narrowly oblong acute sepals 12 to 14 lines long, orange within, greenish yellow without, scarcely exceeding the white narrowly lanceolate acute petals; lip half as long, oblong, somewhat lobed, the thin lateral lobes

veined with purple, the thick middle lobe yellowish with an orange centre and a purple spot without on each side near the undulate margin: column white, shorter than the lip, margined.— In the forests of the Rio Dulce; in flower at Cambridge, November, 1887.

Among other orchids brought by me from eastern Guatemala, which have flowered at Cambridge, have been Restrepia peduncularis, Benth., Stelis ciliaris, Lindl., a variety (?) of Gongora quinquenervis, Ruiz & Pavon, Diacrium bigibberosum, Benth. & Hook., Epidendrum alatum, Batem., E. aciculare, Batem., E. cochleatum, Linn., E. nocturnum, Linn., Schomburgkia tibicinis, Batem., and variety, Oncidium luridum, Lindl., Catasetum maculatum, Kunth, Cycnoches ventricosum, Batem., Lycaste aromatica, Lindl., Chysis lævis, Batem., etc.

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GYMNOLOMIA TPILOBA, Gray. This species has been distributed under the name of *Zaluzania triloba*, Pers., in Mr. Pringle's collections of 1886 (n. 755) and 1887 (n. 1310).

### XVIII.

# CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY.

# WAVE-LENGTHS OF METALLIC SPECTRA IN THE ULTRA VIOLET.

By John Trowbridge and W. C. Sabine.

Presented March 14, 1888.

#### PART L

#### Introduction.

THE Catalogue of Metallic Spectra, revised by a Committee of the British Association, and published in its volumes for 1885 and 1887, is an extremely valuable contribution to the subject of spectrum analysis; it contains the material for future generalization in regard to the molecular structure of so-called elements, or in regard to the harmonic relations which may exist between their wave-lengths. Here can be found in juxtaposition the results of various observers upon the metallic spectra of the same metal, and the student can judge of the relative accuracy of the results. A superficial inspection of this Catalogue will show that even distinguished observers, like Thalen and Kirchhoff, often differ in their results by one part in 4,000, or one part in 2,500. No observer of metallic spectra gives results to more than one tenth of Angstrom's unit, or to more than one tenth of one wave-length. Physical science, however, now demands a greater degree of accuracy. Various hypotheses in regard to the apparent coincidences between lines of metallic spectra and lines in the solar spectrum have been propounded, and can only be settled by more accurate measurements of wave-lengths. There are also questions constantly arising in regard to the displacement of lines of spectra due to the motion of the stars and to changes of temperature, which require a greater degree of accuracy in the measurement of wave-lengths of gaseous and metallic spectra than the results of previous observers afford. It may be remarked, that observations upon the metallic spectra of metals from the limits of the visible red to the limits of the visible violet have become comparatively easy; for the solar spectrum can be used to identify the lines of the metals, and to ascertain their wave-lengths. It is only in the extreme infra red region and in the ultra violet that such observations become difficult. In these regions we must trust to photography to reproduce by long exposures of the sensitive plate the feeble lines of metals which may manifest themselves there. In the infra red region, as far as wave-length 10,000, it is possible to photograph the solar lines, and we can compare the spectra of such metallic lines as may exist between the A line and the limit 10,000 with the solar spectrum. Beyond this limit, and beyond wave-length 2800 in the violet, the solar spectrum disappears, and the problem of measuring the wave-length of metallic lines which extend beyond these limits becomes a difficult one.

Besides the resolution of the difficulty of measuring the wavelengths of the invisible rays of light with proper accuracy, the measurement of such wave-lengths is destined to prove a crucial test for various theories which must arise in the progress of physical science. The lines of the metals are exceedingly numerous in the ultra violet region, far more so than in the infra red region. If there are any harmonic relations between the wave-lengths of the spectra of metals, it is here that one might expect to observe such relations. Professor Grünwald of Prague has lately enunciated a remarkable hypothesis upon the relations between the wave-lengths of so-called elements, and finds in the observations of various observers in the ultra violet a strong confirmation of his hypothesis. In any theoretical work upon the grouping of spectral lines, it is of fundamental importance that the wave-lengths of the lines should be determined with as great accuracy as possible. The coincidence of metallic lines with solar lines is at the best a doubtful piece of evidence. evidence is of moment only when the number of coincidences becomes great, and is accompanied by characteristic grouping. A mistake of a wave-length in the question of position is sufficient to destroy the support which the author of any hypothesis might claim for it.

### Conditions for Accuracy of Measurement.

All measurements of wave-lengths hitherto published have been made by the old method of angular measurements with a spectrometer. We say old, for the use of Rowland's concave grating with its peculiar mounting must be characterized as a new method and a new departure in measurements of wave-lengths. The observation of wave-lengths of metallic spectra by the eye is most laborious, and the photovol. XXIII. (N. S. XV.)

graphic plate must be substituted for the eye for most purposes. angular positions of the spectral lines on such a plate assume great importance, for upon these positions depend the value of the wavelengths. In the operation of photographing spectral lines, it is necessary to substitute, for the observing telescope and micrometer eyepiece of the spectrometer, a camera box provided with a suitable lens, and with a plate holder for the photographic plate. Unless the latter is small, the spectrum will not be in focus on all parts of the plate; moreover, unless the distance of the photographic plate from the diffraction grating employed is comparatively large, the distances between the spectral lines on the photograph will not be proportional to wave-To determine these wave-lengths recourse must be had to The one usually employed is due to Cornu, and can be found described in the Annales de l'École Normale, 2 série, tom. iii. p. 421; also in Journal de Physique, X., 1881, p. 425. It consists in photographing images of the slit of the spectroscope upon the photographic plate, by turning the graduated circle of the spectrometer through measured angles. These photographic images serve as fiducial marks, by means of which wave-lengths of spectral lines on the plate In the case of diffraction spectra obtained by deflecting a bundle of parallel rays at the angle of incidence, i, with a deviation of order n,  $\Delta_n$  is connected to the wave-length  $\lambda$ , and with a certain constant, a, of the grating by the formula

$$2 a \sin \frac{\Delta n}{2} \cos \left(i - \frac{\Delta n}{2}\right) = n \lambda.$$

It is evident that at least two errors can arise in the use of this formula; one from defective graduation of the circle of the spectrometer; another from the process of referring from the photographs of the slit on the plate to the photographs of the metallic lines.

We select the work of Hartley and Adeney \* as perhaps the best type of this method of using a camera with a spectrometer. Their work is characterized by great care and thoroughness, and no one could probably attain better results by the use of a flat grating, with its concomitants of collimator, photographing lens, and camera. These observers state that they were not troubled by the underlying spectrum of a higher order than that which they photographed, for it was not brought to a focus with the latter. In the new method we propose to illustrate, all the spectra are in focus together, and this fact, instead of

<sup>\*</sup> Philosophical Transactions, CLXXV., 1884, pp. 63-137.

being an obstacle, can be turned to great advantage. In the absolute measurements of the wave-length of light, the spectrometer method with eye observation and with a micrometer is unquestionably more accurate than any photographic method. We have in this determination to deal with comparatively large quantities, and with well defined directions, which can be made to coincide with optical axes of the instrument; this is not the case, however, with the majority of the spectral lines on a photographic plate placed in a camera, which replaces the observing telescope of the spectrometer. The photograph contains possible errors, and any shifting or movement of the spectrometer circle to determine intervals on the photographic plate is apt to introduce other errors.

The ideal arrangement would seem, therefore, to be a photographic apparatus which should remain in focus for all the spectra of the different orders, in which distances between successive lines on the photographs of the spectra should be closely proportional to wave-lengths, so that, the constant being known for a certain position of the sensitive plate, the wave-lengths can be determined by simple linear measurement. Moreover, it is desirable, as we have said, that the underlying spectra should be brought to the same focus as the overlying; for by this means we can compare the wave-lengths of lines in the spectra of different orders, and halve our errors. It is true that some confusion results from having the metallic lines in the spectra of different orders photographed upon the same plate; but a little experience enables one to separate the lines with comparative ease, and the gain in accuracy compensates for the additional trouble.

The apparatus which best answers the requisitions we have pointed out is that of the concave grating of Rowland, with its peculiar mounting, which has been fully described in the American Journal of Science, Vol. XXVI., 1883, p. 87.

## Objects of the Present Investigation.

The conclusion of the work of the Committee of the British Association on the tabulation of metallic spectra seemed to us to require a survey of the work, which must be done in the future in order to perfect and correct the work of the past. We have therefore examined the tables given by the committee in order to see what lacunæ could be supplied, and to point out the directions for routine work which may afford material for future generalizations. In the pursuance of this work, we have been compelled to examine the accuracy of measurements of wave-lengths hitherto made in the ultra violet. With

the aid of the new Map of the Solar Spectrum published by Professor Rowland, it is very easy to determine the wave-length of metallic lines in the visible spectra of metals; for it is merely necessary to photograph a portion of the solar spectrum upon the same plate as that which receives the spectra of the metals under consideration, and then to refer to the published map. We have already remarked, that even a superficial examination of hitherto published catalogues of wavelengths of metallic spectra will show that distinguished observers differ in their determinations by one or two wave-lengths. The task of remeasuring the wave-lengths of metallic lines is a very great one, and approaches in character the routine work now prosecuted in astronomical observatories in the redetermination of star places, the photometric intensities of stars, and the classification of star spectra. In our present work we have confined our attention to ultra violet spectra. Since the solar spectrum disappears in the neighborhood of wavelength 2800, the task of identification of wave-lengths becomes a very serious one. To replace the solar spectrum we must refer the lines of metallic spectra to carefully measured lines of certain metals. When one metal ceases to give spectral lines, another must be selected. test the relative accuracy of what we have termed the old method of measurement with that of the new, we have measured the lines of electrolytic copper, and have compared our results with those of previous observers in regard to the distribution of errors. Besides the comparison of accuracy, we have examined the limit of the spectra of copper in the ultra violet, in order to see if that given by previous observers could be extended.

## Apparatus.

The apparatus consisted of a concave grating of 21 ft. 6 in. radius, mounted in the manner described by Professor Rowland. The camera was provided with a shutter, which enabled us to expose different portions of the sensitive plate at pleasure. An alterating dynamo machine was employed, together with a Ruhmkorf coil. The alterating machine gave from eight to ten thousand reversals per second. With a battery of from six to ten two-quart Leyden jars, a powerful spark was obtained between the metallic terminals which we employed. The spark was produced close to the slit of the apparatus, and the time of exposure varied from one to two hours. At various times endeavors were made to substitute the more powerful light of the carbon electric light for the electric spark, in the hope of shortening the time of exposure; but these efforts were not successful. If they had

been, we should have been obliged to struggle with the question of impurities in the carbons. An exposure of fifteen minutes to the ultra violet spectra of metals burned in the electric light produced no image below wave-length 3000. A quartz condensing lens was employed with the arc light, and therefore no light was lost by selective absorption. With the spark no lens was necessary.

By curving the photographic plate all parts of it remain in focus, and distances on the plate are closely proportioned to wave-lengths. Calling Y = wave-length, we have Y = C + a x, where C and a are constants, and x is the distance along the plate.

The determination of the wave-lengths of lines extending over a range of three hundred tenth meters involved the taking of three The sensitive dry plate  $(2 \times 10 \text{ inches})$  was pressed by springs against the "forms" of the plate-holder into an arc of a circle. Having placed the plate-holder on the camera box, the girder bearing the camera and grating was moved along its tracks until the position of the pointer of the carriage on the scale beside the track indicated that light of wave-lengths 4200 to 4800 in the first spectrum and 2100 to 2400 in the second spectrum would fall on the plate. The shutter was turned so as to expose only the lower half of the plate and a photograph of the solar spectrum from 4200 to 4800 The shutter was again turned, and the upper half of the plate given a long exposure to the light of the spark. Both spectra were in The wave-lengths of the metal lines were then found directly, by interpolation on the normal spectrum, from the solar lines whose values were given in Rowland's Photographic Map and table of wavelengths.\* The interpolation was made by means of measurements on a dividing engine. In order to correct for any displacement due to the motion of the spark from side to side, or to jarring arising from the great noise of the spark, and also in order to sift out the lines belonging to the first spectrum from those belonging to the second, the girder was moved to the violet of the third, with its magnified dispersion and different underlying spectra. The metal and solar lines were taken side by side, and the interpolation for the wave-lengths of the metal lines made as before. From this the correction to be applied to the previous plate was found, amounting in some cases to .2 of a tenth meter. The correction thus found was applied to all of the lines on the plate. The girder was now moved so that the sensitive plate was in the extreme ultra violet of the first spectrum, and the plate exposed to the



<sup>\*</sup> American Journal of Science, March, 1887.

light from the spark. From this negative the value of the wavelengths of the faint lines were obtained by interpolation from the values of the stronger lines as determined by the first plate. It also served as the final test whether the lines on the first negative were of the first or second order. All of the lines more refrangible than line 2123.1 were in the case of copper found from this negative and from line 2136.1 by direct measurement.

Another method of distinguishing which lines on the first negative belong to the second and which to the first spectrum, is to place in front of the slit while taking the metal lines a piece of plane glass. The second spectrum for this refrangibility will be completely cut out, and only the metal lines of the first remain, being in the visible violet.

The only source of error was in the setting of the microscope upon the broad or faint lines. The probable error of this is about .1 tenth meter. For the few most refrangible lines it may be greater.

## Effect of Change of Temperature of Source of Light on Constancy of Position of Metallic Lines.

In the process of the investigation we were much troubled by a slight shifting in position of the metallic lines upon the photographs. This shifting could be observed when the metallic lines were compared with a solar spectrum taken upon the same plate. The amount of this shifting in no case amounted to more than .1 or .2 of a wavelength. At first we thought it might be possible that there was a change in refrangibility of the metallic lines due to a difference in temperature of the source of light, and a long study was made of the influence of the temperature of the source of light upon its wave-When a metal was burned in the carbon electric light with varying strength of current, no displacement could be observed between the lines of the metal photographed beneath each other upon the same sensitive plate. When the electric spark with a large battery of Leyden jars was substituted for the electric arc, and the metallic lines obtained by the light of the spark were compared with those from the arc, occasionally a small displacement could be observed. This did not seem to arise from a change of position of the source of light, or from the heating of the slit of the spectroscope. A careful study of the iron lines showed us that the wave-length of the iron lines in the sun and those obtained from burning iron in the electric arc were the same to certainly one hundredth of a wave-length. The displacement we observed was noticed only when the electric spark was employed. This shifting did not arise from a change of position of the spark in

our apparatus, for it could not be produced at will by changing the position of the source of light. Moreover, when the arc light was placed in the same position that the spark occupied, no displacement could be observed in photographs taken by the aid of the arc. We were forced to conclude that through the range of temperature afforded by the electric arc and the electric spark the wave-lengths of the metallic lines were constant. The displacement we observed was therefore referred to a jarring of the apparatus due to the noise of the electric spark. When the camera was at a considerable distance from the slit of the spectroscope, the displacement was diminished, and sometimes entirely disappeared. The entire apparatus was very solid, and the camera was clamped to a massive girder. It was difficult, therefore, to believe that the displacement could arise from the noise of the spark. We believe, however, that it can be ascribed to this cause, and that the wave-lengths of metallic lines produced by burning metals in the electric arc or by vaporization in the electric spark are to one hundredth of a wave-length the same as those of the corresponding lines in the sun.

#### Results.

In the following table we have adopted the same symbols and letters to designate the character of the lines which the Committee of the British Association have employed. Column 1 refers to the intensity on a scale of 10. Column 2 gives our measures of the wavelengths of the copper lines in the ultra violet, from wave-length 2369.9 to 1944.1. Column 3 contains the measures of these lines by Hartley and Adeney. Column 4 are the corrections to be applied to Hartley and Adeney's results. Column 5 contains measurements by Liveing and Dewar. Column 6, corrections to be applied to their results. Column 7 gives the symbols adopted by the Committee of the British Association, which serve to describe the character of the line.



1.	2.	8.	4.	5.	6.	7.
Intensity.	Wave-lengths of copper lines. Spark.	Hartley and Adeney.	Corrections.	Living and Dewar. Arc.	Corrections.	Intensity. B. A.
9	2869.9	2370.1	<b>— .2</b>			9 br
1	2368.8	2368.7	+ .1			2 sd
		2365.8	l			1
4	2356.7	2857.2	5	• • • •		5 sd
3	2355.2	2355.0	+ 2	••••	•••	2 sd
	2848.8	2348.8	. 0	••••	•••	2 sd
1 3	2346.2 2336.3	2346.2 2336. <b>6</b>	8	••••		2 sd 3 sd
100	1	2803.8	8	••••		3 su 1 sd
ï	2299.6	2300.5	9	••••	.:	1 sd
	2200.0	2297.5		••••	::	1 sd
7	2294.4	2295.0	6	2294.1	+.3	6 sd
1	2293.9	2294.6	7	••••	'	8 sd
3	2291.1	2291.4	3			3 sd
3	2286.7	2286.7	0	• • • •		8 sd
2	2278.4	2279.6	-1.2			2 sd
6	2276.8	2277.0	7	2276.0	+.3	6 sd
$\frac{2}{2}$	2265.5	2265.8	8. —	0000.0	l . ;	2 sd
2	2263.9 2263.2	2263.9 2268.2	0 0	2263.6	+.3	8 nd 8 nd
2	2255.1	2208.2 2257.7	-1.6	••••		2 sd
2 2 7	2249.0	2250.0	-1.0 -1.0	••••		2 sd
7	2247.0	2248.2	-1.2	2246.6	+.4	9 sd
		2247.7			1	3 nd
7	2242.7	2244.0	-1.8	2242.2	+.5	9 sd
		2243.5	١		'	3 nd
1	2281.7	2233.0	-1.3	• • • •		3 sd
1	2231.0	2832.2	-1.2			3 sd
3	2230.1	2231.2	-1.1	2229.6	+.5	5 sd
3	2228.9	2230.0	-1.1	2228.8	+.6	5 sd
2	2227.8	2229.1 2228 1	—1.3 —1.2	••••		3 sd 3 sd
1	2226.9 2225.7	2228 1 2227.0	-1.2 -1.3	••••		1 sd
1	2224.8	2226 0	-1.3 -1.2	• • • •		1 sd
6	2218.2	2219.8	-1.1	2217.5	+.7	6 sd
	2010.2	2218 5		221110	1 '::.	3 nd
2	2215.3	2216.5	-1.2		::	8 nd
1	2214.4	2215.8	-1.4			3 sd
2	2218.0	2214.1	-1.1	••••		2 sd
6	2210.3	2211.3	<b>—1.0</b>	2209.7	+.6	6 sd
		2210.8	•••	••••		3 nd
2	2000.0	2208.8	1	••••	• • •	2 sd
3	2200.6 2199.8	2200.3 2199.8	+ .8	2199.2	<u>ن</u> ا	3 sd 1 nd
3	2196.9	2199.5 2196.5	+ .4	2100.2	+.6	nd 8 ad
4	2192.4	2192.0	I ¼	2191.8	+.6	6 ad
	2102.2	2191.2	''.:-		7.0	8 nd
4	2189.9	2189.6	+ .8	2189.2	+.7	6 sd
		2188.5	'	••••	'".	8 nd
1	2181.8	2181.0	+ .8	••••	•	1 sd
4	2179.5	2179.0	+.5	2178.8	+.7	5 sd
		2178.0	l . • <u>-</u>	••••	••	8 nd
3	2175.2	2174.5	+ .7	••••		3 sd

1. Intensity.	2. Wave-lengths of copper lines. Spark.	3. Hartley and Adeney.	4. Corrections.	5. Liveing and Dewar. Arc.	6. Corrections.	7. Intensity. B. A.
3 4 3 3 8 8 3 2 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 1 1 1 1 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 1 2 2 2 2 2 1 1 1 1 2 2 2 2 2 1 1 1 1 1 1 2 2 2 2 2 1 1 1 1 1 1 2 2 2 2 2 1 1 1 1 1 1 2 2 2 2 2 1	2149.2 2136.1 2134.6 2126.2 2125.3 2123.1  2117.5 2112.2 2104.9 2098.6 2093.9 2088.1 2085.5 2078.8 2067.0 2062.7 2055.1 2045.0 2037.3 2036.0 2030.9 2016.8 2015.8 2013.2 1999.9 1988.4 1970.4 1970.4	2148.8 2135.8 2134.2 2124.4 2124.0 2122.1 2121.5 2116.0 2110.5 2103.0	+ .4 + .3 + .4 + 1.8 + 1.0 + 1.5 + 1.7 + 1.9	2148.9 2185.7 	+.3 +.4  	3 sd 3 sd 2 nd 3 sd 2 nd 1 sd 1 sd

### Conclusions.

It will be observed that the corrections to be applied to the wavelengths obtained by Liveing and Dewar are progressive in their nature when compared with those which must be applied to the results of Hartley and Adeney. The difficulty in identifying lines and determining coincidences by employing the tables of metallic spectra in the ultra violet, published by the British Association, is illustrated by our work; for certain lines measured by Liveing and Dewar, which are identified by the committee with lines given by Hartley and Adeney, are in reality removed from each other, one or two lines intervening. In certain cases the lines of Liveing and Dewar are wholly beyond identification with those given by Hartley and Adeney.

The results of our inquiry into the accuracy of the results of previ-



ous observers in measuring wave-lengths of metallic spectra in the ultra violet can be summed up as follows.

- 1. We believe that the method of photographing images of the slit upon the photographic plate, due to Cornu, in order to determine positions, leads to unavoidable errors.
- 2. The best method of determining wave-lengths of metallic spectra is by the use of concave gratings; for linear measurements are substituted for angular ones; underlying spectra are brought to the same focus as overlying spectra; and, since a great number of lines are in focus on the same plate, the conditions are the same for all, viz. breadth of slit, length of exposure, and source of light.
- 3. Hypotheses in regard to coincidences of gaseous and metallic spectra cannot be safely based upon existing measurements of spectra in the ultra violet.
  - 4. The limit of the copper lines is extended by our investigation.

#### XIX.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY.

SELECTIVE ABSORPTION OF METALS FOR ULTRA
\* VIOLET LIGHT.

By John Trowbridge and W. C. Sabine.

Presented March 14, 1888.

THE question of the absorption of the ultra violet rays by metallic surfaces possesses considerable interest, both from a practical and a theoretical point of view. By the kindness of Professor Pickering, Director of the Harvard University Observatory, we were provided with a number of metallic surfaces prepared by Professor Wright of Yale College. These metallic surfaces were deposited upon glass by means of electricity. The surfaces were of gold, platinum, tellurium, palladium, copper, silver, and steel. A preliminary trial had shown us that a heliostat mirror of the same composition as that upon which the grating was ruled did not absorb light of greater wave-length than 2900. We resolved, therefore, to compare other metals with specu-Since our heliostat arrangement required two mirrors to lum metal. direct the light upon the slit of the spectroscope, we employed a speculum mirror for the movable mirror of the heliostat, and replaced the fixed mirror by mirrors of the metals whose selective absorption we wished to compare with that of speculum metal. To our surprise, the metallic mirrors of gold, copper, nickel, steel, silver, tellurium, and palladium all reached the same limit as speculum metal. a complete experimental proof that color in no way influences the selective absorption of metals for the ultra violet rays; for the copper mirror, which gave a strong yellow light by reflection, was as capable of reflecting light of as short wave-length as the brilliant white surface of polished silver. Although the metallic surfaces we employed were bright, slight differences in polish undoubtedly existed, and therefore we are not justified in placing much reliance upon the evidence presented by the intensity of the photographs of the solar spectrum obtained by light reflected into the spectroscope by these various metallic surfaces. The photographs, however, can be classified according to intensity in order of numbers as follows, — number 1 indicating the greatest intensity: 1, steel; 2, gold; 3, platinum; 4, palladium; 5, silver; 6, tellurium; 7, copper.

It was evident from these experiments that the selective absorption of metals is far less than the absorption exercised by the earth's atmosphere. We therefore resolved to employ the light of the electric spark between metallic terminals, in order to ascertain whether any limit of absorption could be reached. For this purpose, the light of the spark between copper terminals was reflected, by means of a mirror of the metal whose selective absorption we wished to examine, upon the slit of the spectroscope. To protect the surface of the mirror from the effects of the spark, a thin plate of quartz was placed in front of It was found that the copper mirror showed no limit of selective absorption by reflection for wave-lengths of light produced by burning copper at the limits of the copper spectrum, that is, at wave-length 2100. The photographic plate taken by this method showed all the lines that the plates showed which were taken by the direct light of the spark unreflected and unabsorbed by any medium. The palladium mirror was substituted for the copper mirror, and also showed no limit of selective absorption above wave-length 2100. We are led to conclude, therefore, that the metallic surface of the speculum metal upon which the lines are ruled which form the diffraction grating does not fix by selective absorption the limit of metallic spectra at This limit more likely resides in the materials forming the sensitive emulsion with which the sensitive plates are coated. We have found that a marked difference exists in different emulsions in regard to sensitiveness to ultra violet light. The various staining processes, which enhance to such a marked degree the sensitiveness of photographic plates to wave-lengths of greater length, do not seem to affect the limit of metallic spectra in the ultra violet. Thus, plates stained with erythrosine, which are extremely sensitive to yellow and green light, continue to give the same limit in the ultra violet after staining as they did before they were submitted to the staining process.

#### XX.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY.

# PHOTOGRAPHY OF THE LEAST REFRANGIBLE PORTION OF THE SOLAR SPECTRUM.

By J. C. B. BURBANK.

Presented by Professor Trowbridge, March 14, 1888.

It has been stated by eminent authorities, that the process of staining dry plates with various dyes is not applicable to the photography of the invisible rays beyond the red of the solar spectrum. To test this question I have undertaken a series of experiments with the dye cyanine. This dye has of late come into considerable prominence in photography, owing to its orthochromatic effect when mixed with other dyes, such as chinoline-red, azaline, erythrosine, and eosine.

It was discovered by Greville Williams, an Englishman, in 1861, but did not come into much prominence until the year 1884, when its usefulness as a sensitizer became more apparent. The dye is easily decomposed by light, and even in the dark both its solution and the plates coated with it are apt to become decomposed if kept for any length of time. Alone, it has been found very useful to sensitize plates for the orange and red portions of the spectrum. No experiments have to my knowledge been made upon the effect of heat rays upon cyanine plates.

The direct action of absorbents in the infra red has not, hitherto, been tried with any success; moreover, it has been stated by so eminent an authority as Captain W. De W. Abney that it was impossible to make plates sensitive to any rays below the A of the solar spectrum by means of the addition of dyes to a film. It is true, however, that Major Waterhouse has succeeded by means of turmeric in obtaining evidence of the existence of a few lines on the less refrangible side of A, but in all cases except one these were reversed.

The plates employed were made by the M. A. Seed Co. of sensitometer 22. The method used in staining the plates and in the prepa-

ration of the dye is substantially the same as that employed by J. B. B. Wellington,\* and is as follows.

Fifteen grains of cyanine are gently heated (over a steam bath) for from thirty to forty minutes in combination with 1 oz. of chloral hydrate and 4 oz. of water. The whole mixture should now be stirred vigorously. While this operation is going on, 120 grains of sulphate of quinine are dissolved by heat in a few ounces of methylated spirit. (If methylated spirit cannot be obtained, a solution of 90% alcohol and 10% wood spirits will answer perfectly well.) One ounce of strong aqua ammonia is now slowly added to the cyanine mixture above. Violent ebullition takes place immediately, chloroform being evolved, and cyanine is deposited in a soluble form on the sides of the vessel. The mixture is allowed to settle for a few minutes, and then the supernatant liquid is decanted off very slowly, care being taken not to detach any of the cyanine that is formed on the sides.

To the remaining cyanine, three or four ounces of methylated spirit are added to dissolve the cyanine; the quinine solution is then added; and to the whole more methylated spirit, until the whole mixture measures from eight to nine ounces. This solution constitutes the "stock" solution, and should be kept away from all light, as it is very apt to become decomposed.

All of the above operations should be conducted in as little light as possible. The following staining and drying processes should be conducted in absolute darkness.

To thirty ounces of water are added  $1\frac{1}{2}$  drachms of the cyanine stock solution; the graduate that contained the cyanine is now washed out,  $1\frac{1}{2}$  drachms of strong aqua ammonia are added, and the whole mixture is stirred vigorously. Into this bath two or three plates, or half a dozen strips, can be dipped at once. They should be left there about four minutes; meanwhile the tray containing the plates should be rocked continuously, so as to insure a uniform action of the dye.

This bath, after having been used once, should be thrown away, as the action on a second batch of plates would be weak and imperfect. The plates can now be drained, dried, and used. While developing, I was careful to exclude all light whatever, although I think it possible that the plates may be developed safely in a dark greenish yellow light. The developer used was a pyro. and potash developer of (generally) normal strength.

<sup>\*</sup> See Anthony Photographic Bulletin, December 24, 1887.

In the first experiments the spectrum was produced by a Rowland flat diffraction grating, mounted on a spectrometer circle. This grating contained 17,000 lines to the inch. The observing telescope of the spectroscope was replaced by a camera and lens.

Certain photographs were also taken by means of a Rowland concave grating of 14,500 lines to the inch, and of 21 ft. 6 in. radius of curvature. With this grating, the amount of light being less and the dispersion greater than in the former cases, the exposure had to be increased.

In all of the experiments ruby-red glass screens were used in order to cut out all of the more refrangible part of the underlying spectrum. In some cases a weak solution of iodine in carbon disulphide was used with good effect.

No difficulty was found in photographing from the A line to wavelength 9900, or to the limit assigned by Abney as the limit of the diffraction spectrum. None of the lines were reversed. A special study of the A group was made, photographs being taken at different seasons in order to see if any changes in the remarkable group of lines constituting the A group could be noticed. No existing map represents this group correctly. Employing the second spectrum produced by a concave grating, 52 lines were observed between wave-lengths 7100 and 8000. In the same space Abney records only 24 lines. Between the head of A and the tail of A, the latter being the single line before the series of doublets begin which is so characteristic of the A group, my photographs show 17 lines. These photographs were taken in June between ten and one o'clock.

These results are of special interest when we consider that Abney has said in a Bakerian lecture, "As a result of these experiments I can confidently state that in no case did the addition of a dye cause any chemical effect to be produced by the rays below A of the solar spectrum, nor has Vogel claimed that they do."

It is interesting to note that Abney is led to believe that the photographic action, which has been noticed hitherto, by the use of dyes as sensitives, can be attributed to a certain action of nitrate of silver on organic matter. This effect is a bleaching one, and only the more fugitive dyes can produce it. We are led to conclude from Abney's paper, that he believes that only a chemical effect produced in a specially prepared emulsion can be used to reproduce the infra red rays. After many experiments he succeeded in producing such an emulsion. The color of this verged upon the blue. Since the color of plates

stained with cyanine by the process I have described is also blue, there may be some physical significance in this resemblance.

My experiments show that a specially prepared emulsion is not necessary for the photography of the infra red region. The chemical theory advanced by Abney, therefore, seems to need revision.

### PROCEEDINGS.

#### Eight hundred and third Meeting.

May 24, 1887. — ANNUAL MEETING.

The President in the chair.

The Corresponding Secretary read the following letters: from Messrs. Martin Brimmer and J. Walter Fewkes, accepting Fellowship; from Professor William R. Ware, accepting Associate Fellowship; from the Hon. Frederic W. Lincoln, resigning his Fellowship. A letter was read announcing the death, on the 2d instant, of Professor Bernhard Studer, of Bern, Foreign Honorary Member, at the age of ninety-three years.

On the motion of the Corresponding Secretary, it was *Voted*, To meet, on adjournment, on the third Wednesday in June, at eight o'clock.

The Reports of the Treasurer and Librarian were read and accepted.

The following papers were presented: —

"Acoustic Submarine Signals: for Use on Steam Vessels in Foggy Weather." By John M. Batchelder.

"Measurements of Telephonic Currents produced by a Blake Transmitter with varying Pressure." By Charles R. Cross.

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#### Eight hundred and fourth Meeting.

June 15, 1887. — ADJOURNED ANNUAL MEETING.

The PRESIDENT in the chair.

In the absence of Professor Watson, Professor Putnam was appointed Secretary pro tempore.

The President made a brief statement of the indebtedness of the Academy to its late Fellow, Daniel Treadwell, and suggested that a special appropriation should be made for printing a memoir of Mr. Treadwell.

On the motion of the Treasurer, it was

Voted, That an appropriation of four hundred dollars (\$400) be made for printing a memoir of Daniel Treadwell, by Dr. Morrill Wyman.

On the motion of the Treasurer, it was

Voted, To appropriate from the income for the ensuing year: —

For general expenses	•	•	•		•	<b>\$2,200.00</b>
For publications						2,000.00
For the library						1,000.00

The President read the following report.

The Rumford Committee present the following report for the year ending with this Annual Meeting: —

An appropriation of \$500 was made to Professor H. P. Bowditch to enable him to construct a calovimetric apparatus for physiological investigations.

An appropriation of \$250 was made to Professor Trow-bridge for investigations on radiant energy.

An appropriation of \$250 was made to Professors Cross and Holman, for new researches in thermometry; and an appropriation of \$75 for experiments on the effect of thermoelectric and other thermal actions upon the accuracy of the Munich-shunt method of measuring very strong currents of electricity.

An appropriation of \$250 is recommended for the use of Mr. E. D. Leavitt, Jr., for work on pyrometry and other

methods of measuring high temperatures, to be done in connection with Professor Trowbridge.

The Treasurer has paid from the income of the Rumford Fund \$368.50 for the Rumford Medals, \$500 to Mr. W. H. Pickering, to aid him in observing the total eclipse of the sun in August, \$250 to Professor Trowbridge for his research, \$149.05 for books and journals on light and heat, and \$463.13 for printing in the Memoirs or Proceedings papers relating to these subjects. Appropriations to the amount of \$825 have not yet been paid and will come out of the income of the current year.

The Committee ask the Academy to act upon the annexed vote.

#### For the committee.

JOSEPH LOVERING, Chairman.

Voted, That an appropriation of \$250 be made from the income of the Rumford Fund to aid Mr. E. D. Leavitt, Jr. in his work on pyrometry and other methods of measuring high temperatures.

The report was accepted and the Academy passed the vote recommended by the committee.

Professor Cooke presented the Annual Report of the Council.

The President read a letter from Dr. O. W. Holmes, in which he declined re-election to the office of Vice-President; also, a letter from Professor C. R. Lanman, Corresponding Secretary of the American Oriental Society, thanking the Academy for the use of its Hall for the meeting of the Society.

Dr. William Everett read a notice of the Hon. Charles Francis Adams, late President of the Academy, which he had prepared at the request of the Council.

Dr. Everett stated that on the 4th of July a memorial service would be held in Quincy in honor of Mr. Adams.

The Corresponding Secretary announced that memorial notices had been prepared, by the request of the Council, of Mr. Charles C. Perkins, by the Hon. Martin Brimmer, and of



Professor William R. Nichols, by Professor Francis H. Storer, and that they would appear in the Proceedings.

The following gentlemen were elected members of the Academy: —

Winfield Scott Chaplin, of Cambridge, to be a Resident Fellow in Class I., Section 4.

Eliot Channing Clarke, of Boston, to be a Resident Fellow in Class I., Section 4.

The annual election resulted in the choice of the following officers: —

JOSEPH LOVERING, President.
FRANCIS PARKMAN, Vice-President.
JOSIAH P. COOKE, Corresponding Secretary.
WILLIAM WATSON, Recording Secretary.
AUGUSTUS LOWELL, Treasurer.
HENRY W. HAYNES, Librarian.

#### Council.

WOLCOTT GIBBS,
CHARLES L. JACKSON,
CHARLES R. CROSS,
Of Class I.

SERENO WATSON,
ASA GRAY,
HENRY W. WILLIAMS,

Of Class II.

JOHN C. ROPES,
FREDERICK W. PUTNAM,
JUSTIN WINSOR,

of Class III.

## Rumford Committee.

WOLCOTT GIBBS, JOSIAH P. COOKE, EDWARD C. PICKERING, JOSEPH LOVERING, JOHN TROWBRIDGE, GEORGE B. CLARK, ERASMUS D. LEAVITT, JR.

Member of the Committee of Finance.

THOMAS T. BOUVÉ.

The President appointed the following standing committees: —

Committee of Publication.

JOSIAH P. COOKE, ALEXANDER AGASSIZ,
ASA GRAY.

Committee on the Library.

HENRY P. BOWDITCH, AMOS E. DOLBEAR, EDWARD J. LOWELL.

Auditing Committee.

HENRY G. DENNY, THOMAS T. BOUVÉ.

The following papers were presented: -

- "The Relative Values of the Atomic Weights of Hydrogen and Oxygen." By Josiah P. Cooke and Theodore W. Richards.
- "Summary of the Observations of the Total Eclipse of the Sun, August 29, 1886." By William H. Pickering.

The following papers were presented by title: -

- "The Action of Fluoride of Silicon on Organic Bases." By Arthur M. Comey and C. Loring Jackson.
- "On Tribromtrinitrobenzol." By C. Loring Jackson and John F. Wing.
- "Catalogue of all Recorded Meteorites, with a Description of the Specimens in the Harvard College Collection, including the Cabinet of the late J. Lawrence Smith." By Oliver W. Huntington.

#### Eight hundred and fifth Meeting.

October 12, 1887. — STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of the following members:—

Alvan Clark, Mark Hopkins, and Charles E. Ware, Resi-

dent Fellows; Spencer F. Baird, Associate Fellow; Hugh A. J. Munro, Foreign Honorary Member.

Voted, To meet, on adjournment, on the second Wednesday in November.

Professor Charles R. Cross presented the following papers: —

- "On the Inverse Electromotive Force of the Voltaic Arc containing Volatilized Salts."
- "Further Studies of the Melting Platinum Standard of Light."

#### Eight hundred and sixth Meeting.

November 9, 1887 — ADJOURNED STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of Gustav Kirchhoff, of Berlin, Foreign Honorary Member.

Professor Truman H. Safford presented the following papers: —

- "On the Approach of the North Pole and the Polar Star."
- "On the Right Ascension of Stars near the North Pole, observed at Williamstown, Massachusetts, (Field Memorial Observatory,) in the Year 1885."

The following paper was presented by Professor Trowbridge: — .

"A Preliminary Investigation of the Velocity of Sound in Liquids." By Harold Whiting.

#### Eight hundred and seventh Meeting.

December 14, 1887. — MONTHLY MEETING.

The PRESIDENT in the chair.

Professor Holman presented a paper entitled, "Boiling Points of Naphthaline, Benzophenone, and Benzol under controlled Pressures, with special Reference to Thermometry." By Silas W. Holman and Walter H. Gleason.

#### Eight hundred and eighth Meeting.

January 11, 1888. — STATED MEETING.

The PRESIDENT in the chair.

Voted, To meet, on adjournment, on Wednesday, February 8, 1888.

Professor Cross presented the following papers: -

- "Experiments on the Blake Microphone Contact." By George W. Patterson, Jr., and H. J. Tucker.
- "On Possible Sources of Error in the Permanent-shunt Method of measuring the Strength of Currents." By William L. Puffer.

Professor William L. Hooper made a communication on a new form of standard resistance coil.

#### Eight hundred and ninth Meeting.

February 8, 1888. - ADJOURNED STATED MEETING.

A quorum was not present, and the Academy was not called to order.

#### Eight hundred and tenth Meeting.

March 14, 1888. — STATED MEETING.

The President in the chair.

The President announced the death of Asa Gray.

The following gentlemen were elected members of the Academy:—

Abbott Lawrence Rotch, of Boston, to be a Resident Fellow in Class I., Section 3.

Elihu Thomson, of Lynn, to be a Resident Fellow in Class I., Section 3.

George Fillmore Swain, of Boston, to be a Resident Fellow in Class I., Section 4.

Crawford Howell Toy, of Cambridge, to be a Resident Fellow in Class III., Section 2.

On the recommendation of the Rumford Committee, it was

Voted, To appropriate two hundred and fifty dollars (\$250) from the income of the Rumford Fund to assist Professor Trowbridge in his work on metallic spectra.

The following papers were presented: -

- "Historical Study at Babylon in the Sixth Century B. C." By David G. Lyon.
- "An Instrument for determining the Direction and Velocity of Water Currents below the Surface." By Edward S. Ritchie.

The following papers were presented by title: -

- "On Sulphopyromucic Acids." By Henry B. Hill and Arthur W. Palmer.
- "Notes upon some Polypetalous Genera and Orders." By Asa Gray.
- "Contributions to American Botany: I. Some New Species of Plants of the United States. II. Some New Species of Mexican Plants, chiefly of Mr. C. G. Pringle's Collection in the Mountains of Chihuahua, in 1887. III. Description of some Plants of Guatemala." By Sereno Watson.

Mr. Sereno Watson exhibited and described a specimen of wild corn found in the mountains south of Guanaxuato in Mexico.

#### Eight hundred and eleventh Meeting.

April 11, 1888. — MONTHLY MEETING.

The President in the chair.

The following papers were presented: —

- "The Proper Shape for Armature Cores in Dynamo-electric Machines." By William L. Hooper.
- "Results of the Comparison of a Number of British Association Standards of the Units of Electrical Resistance." By William L. Hooper.



#### Eight hundred and twelfth Meeting.

May 9, 1888 - Monthly Meeting.

The President in the chair.

In the absence of the Recording Secretary, Mr. Haynes was appointed Secretary pro tempore.

The Corresponding Secretary read letters from Messrs. Rotch and Thomson, accepting Fellowship in the Academy; from the General Secretaries of the International Geological Congress, inviting the attendance of members of the Academy at the approaching meeting in London, in September; from the President of the American Philosophical Society in regard to a proposed international congress to consider the subject of a universal language; from the Audubon Monument Committee of the New York Academy of Sciences, soliciting subscriptions; from a committee in the Netherlands inviting subscriptions to the "Donders memorial fund."

The First Part of Volume XXIII. of the Proceedings was laid on the table.

The following papers were presented: —

- "A Note on the Atomic Weight of Oxygen." By Josiah P. Cooke.
- "On the Present Condition of the Subject of Color; together with an Account of Investigations at the Jefferson Physical Laboratory on the Invisible Rays of Light." By John Trowbridge.
- "Result of Studies of the Strength of Electric Currents used in Telegraphy and in Microphones." By Charles R. Cross.



# REPORT OF THE COUNCIL:

#### MAY 23, 1888.

SINCE the last Annual Meeting, on May 24, 1887, the Academy has received notice of the death of fifteen of its members; — viz. seven Resident Fellows, Alvan Clark, Charles S. Bradley, John Dean, Asa Gray, Laurens P. Hickock, Mark Hopkins, Charles E. Ware; three Associate Fellows, S. F. Baird, S. G. Brown, and E. B. Elliott; and five Foreign Honorary Members, Matthew Arnold, Henry Sumner Maine, H. A. J. Munro, Gustav Kirchhoff, and Balfour Stewart.

#### RESIDENT FELLOWS.

#### ALVAN CLARK.

ALVAN CLARK was born in Ashfield, Massachusetts, on March 8, 1804. The unusual capacity for delicate manipulation which subsequently established his reputation as an optician first displayed itself in a taste for painting. His youth was passed in labor on the farm of his father, but before he was twenty-two he had acquired much skill in his favorite art. Circumstances required him to make a practical use of this skill, for the New England of 1826 could offer little encouragement to æsthetic pursuits, and Mr. Clark exchanged farming for engraving the rolls used for printing calico in a manufactory at Lowell. But in 1835 he ventured to establish himself in Boston as a portrait painter, and pursued that business for the next twenty years, his residence being in Cambridge. He had married while living at Lowell,

<sup>\*</sup> A notice of Elliott could not be prepared for this volume; but notices of Curtius, Eichler, and Studer, necessarily omitted last year, are now given.

and his eldest son, by undertaking the construction of a small reflecting telescope as a juvenile experiment, first directed his attention to optical work. The occupation, once begun, proved too interesting to be laid aside, but some time necessarily passed before astronomers began to discover the surprising excellence of the instruments which were produced by a maker who had received no professional training as an optician, and had reached middle life without intending to become one. Mr. Clark began the manufacture of telescopes at Cambridge in 1846. with the aid of his two sons, and proved the superiority of his work by astronomical observation, during which he discovered several double stars, requiring, on account of the close proximity of their components, an instrument of unusual defining power for the recognition of their character. His correspondence upon this subject with the distinguished English observer of double stars, the Rev. W. R. Dawes, led to the purchase by Mr. Dawes of some of his telescopes, and to the growth of his reputation among other astronomers. His portrait painting was laid aside, to be resumed only as the recreation of his old age, when it appeared that his eye and hand still preserved the accuracy which had distinguished his youth. As an additional illustration of this accuracy, it may here be mentioned that, during the prime of life, Mr. Clark took much interest in practice with the rifle, and greatly distinguished himself as a marksman. To render assistance in loading the rifle with accuracy, he invented a false muzzle, which is still employed among those who have not adopted the breech-loading guns which are now in common use.

By degrees it appeared that the firm of Alvan Clark and Sons was indisputably at the head of the telescope makers of the world, notwithstanding an entire neglect of all the arts of business competition. became necessary for aspirants to the possession of a telescope superior to any which had been previously made, to resort to the works at Cam-In 1860, the University of Mississippi ordered a telescope eighteen inches in aperture. The outbreak of civil war the next year changed the destination of this instrument to Chicago; but, before it left Cambridge, the companion of Sirius, a body previously known only in theory, was discovered with its aid. In 1877, with the twenty-sixinch refractor of the United States Naval Observatory, also the work of Alvan Clark and Sons, and the largest instrument of its class then mounted, the two satellites of Mars were discovered. The great Russian Observatory of Pulkowa next demanded a still larger instrument, and finally the Lick Observatory of California called for one even greater. This was the last important work of the firm which he had



founded that Mr. Clark lived to witness. He died after a short illness, at the age of eighty-three. Few men can have such good reason to enjoy either the active or the retrospective portions of their lives as had Alvan Clark, and few have seemed really to enjoy their opportunities of promoting science more than he did. His genial and kindly temperament will long preserve his memory among those who saw him in his later years, surrounded by the implements of the work which he loved to the last.

#### CHARLES SMITH BRADLEY.

CHARLES SMITH BRADLEY, formerly Chief Justice of Rhode Island, became a Fellow of the Academy on October 10, 1877. He was the son of Charles and Sarah (Smith) Bradley, and was born at Newburyport, Mass., July 19, 1819. His father was a merchant of Boston, and afterwards a manufacturer, residing at Portland, Maine; on his mother's side he was descended from the Rev. Dr. Hezekiah Smith, for many years a Baptist preacher and a Fellow of Brown University; and so, after preparing for college at the Boston Latin School, he completed his education at Brown University, and graduated there in 1838 at the head of a distinguished class. Of his own distinction in college a pleasant picture is given by a contemporary, in Mr. Charles T. Congdon's "Reminiscences of a Journalist," Boston, J. R. Osgood & Co., 1880): "In the class of 1838 was Mr. Justice Bradley of Rhode Island, the first scholar, I think, of his year, of whom we did predict great things. There is something pleasant in the loyal way in which lads in college recognize an associate of superior ability and special promise. . . . So we all talked of Bradley. When he was to speak in the chapel after evening prayers, how irreverently eager we were for the devotions to be over that we might listen to our favorite! There were other clever fellows, of course, but none so clever as he. He handled all topics, philosophical, political, and literary, with such force and ease that we held the matter hardly second to the manner, though the manner was as nearly perfect as any elocution could be; yet there were doubters who thought that George Van Ness Lothrop, now an eminent lawyer of Michigan, was, if possible, the greater man. Of the comparative merits of these two, the discussions ran high, but there was no discussion of the rival claims of anybody else." Mr. Lothrop was the first Minister to Russia under President Cleveland, and one of Judge Bradley's sons now bears his name.

He studied law at the Harvard Law School, and at Providence in



the office of Charles F. Tillinghast, whose partner he became on being admitted to the bar of Rhode Island, in 1841. He was soon eminent in his profession, and for many years was one of its acknowledged leaders. In politics he was always a Democrat. It was therefore a very striking mark of appreciation which was shown when he was elected Chief Justice of the Supreme Court by the Republican legislature of Rhode Island, in February, 1866. He filled this office with distinction for two years, resigning it then on account of the pressure of his private affairs. Soon after this, he was for several years one of the lecturers at the Harvard Law School, and in 1876 he succeeded the Hon. Emory Washburn as the Bussey Professor at that institution, and held the office for three years. He was called to many other places of honor and service. He was a member of the State Senate of Rhode Island, and a Fellow of Brown University. He repeatedly led the forlorn hope of the Democratic party in Rhode Island as a candidate. for the national House of Representatives and Senate, and as a member of the National Convention of that party.

He was a man of learning and of wide accomplishments, and of spotless integrity and honor. As a lawyer, he had an extraordinary quickness of apprehension, subtlety, fertility of resource, great native breadth of good sense, and a vigorous understanding. He was a lover and student of literature, and especially of art; and there was in him what one of his friends has happily called "a certain elegance about his intellectual structure and movement, a mixture of grace and sentiment and imagination with his logical and practical power, which lifted him above the dry professional road he travelled by choice, and with so much success." From the beginning he had always a great charm of manners and character. In earlier life he was very slender, and his aspect was that of a refined and thoughtful scholar. Later on, his tall figure grew fuller, but never unwieldy; and his handsome face, and his head silvered with age, became noble, and expressive of strength, dignity, and repose.

He was accomplished as a public speaker, — indeed, he came near being a very finished and remarkable orator. Public speaking was easy to him. In preparing for it he wrote little, speaking mainly without notes or from slight memoranda. His oration before the Phi Beta Kappa Society at Cambridge, in 1879, was never written out; he trusted largely to the inspiration of the moment, as was his wont. Several of his addresses, however, were reported, and have appeared in print. The last of them, on "The Profession of the Law as an Element of Civil Society," was delivered at the University of Virginia, in 1881.

He was a good citizen and gave much time and reflection to public questions; and his course was always a thoughtful and independent one. Although supporting the "Law and Order" side at the time of the Dorr rebellion in Rhode Island, he was persuaded of the injustice and bad policy of many of the steps that were taken by the victorious party, and courageously opposed them by tongue and pen. last he struggled earnestly to remove from the Constitution of Rhode Island certain features which seemed to him inexpedient and unjust; and it was in the course of this controversy that he was led to a careful study of the methods of making and changing the constitutions of our States, which resulted in a series of newspaper articles printed at Providence, and afterwards embodied in a learned and very valuable, although somewhat ill-constructed pamphlet. The main conclusions arrived at by Chief Justice Bradley were not welcomed by the judges of the Supreme Court of Rhode Island, whose opinion he controverted, or by the prevailing political party there, and he was answered by Chief Justice Durfee of that State; but those conclusions are well worthy of attention. They have the support of many eminent persons, and among others of Jameson, the author of the principal treatise on the subject of "Constitutional Conventions."

Chief Justice Bradley died at the Buckingham Hotel, in the city of New York, April 29, 1888. Although successful in business and fortunate and happy in many of the aspects of his life, he had much more than the usual share of domestic sorrow that falls to man's lot. He was thrice married, and each time happily; yet he survived for thirteen years the last of his wives. The loss of all his daughters in their infancy was a sad blow to a man of a nature singularly affectionate and sensitive. Two sons, also, the oldest and the youngest, who had grown to be men, died before him. Two sons survive him, Charles Bradley of Providence, and George Lothrop Bradley of Washington. He left a handsome property, but made no will. During all the later part of his life he was an attendant at the Episcopal Church. A portrait of him by Herkomer taken a few years before his death is in the possession of his son George.

#### JOHN DEAN.

JOHN DEAN, the son of William and Lydia Dean, was born at Salem, Mass., December 21, 1831. He was educated in private schools, and did not go to college, but went abroad for a year or two in 1850. He studied chemistry with Professor Horsford, in the Harvard Scientific



School, in 1852-53, and soon afterward went to Germany to pursue his studies in that science. He took the degree of Ph. D. at the University of Göttingen. He entered the Harvard Medical School in 1856, and graduated in 1860. There is still in the Museum a beautiful dissection of nerves bearing his name and that of Charles F. Crehore. During his medical course he must have found time for original research; for his first important work, on the "Lumbar Enlargement of the Spinal Cord," was presented before the Academy of Arts and Sciences, by Prof. Jeffries Wyman, on November 14, 1860. A still larger work, illustrated by photographs of his sections as well as by plates, was that on the "Gray Substance of the Medulla Oblongata and Trapezium," published by the Smithsonian Institution in 1864. His reputation was thus made, and in a field which in America, at least, was absolutely new. Unfortunately his health now failed him. He suffered from nervous exhaustion, and from chronic bronchitis and asthma, from which after that time he was rarely free, and which repeatedly brought him into a critical condition. For many years he was a complete invalid.

He married, in 1859, Miss Eliza Philbrick Southwick, whose care of him was tender and constant till his death. He went abroad for several years, and made several fruitless attempts to resume his work. At last, feeling that his case was hopeless, some twelve years ago, being at that time in America, he gave his entire scientific library, which contained files of valuable scientific periodicals and many rare and costly works on the nervous system, his instruments, and a choice collection of microscopic specimens to the Physiological Department of the Harvard Medical School. He went abroad for the last time in the spring or summer of 1882, and from that time made his home in Florence, where he died on January 13, 1888.

It was a severe blow to him to give up his scientific labors; but he bore it with characteristic patience, and took pleasure in thinking that he had so disposed of his books and preparations that they would be of use to others. Dr. Dean was of a most amiable character, — affectionate, modest, and submissive. Many years ago, both Dr. and Mrs. Dean became converts to the Roman Catholic Church, of which he died a zealous and devout member. \*

<sup>\*</sup> Abbreviated from a notice in the Boston Medical and Surgical Journal.

#### ASA GRAY.

Asa Gray was born on November 18, 1810, in Sauquoit Valley in the township of Paris, Oneida Co., N. Y., and died on January 30, 1888, at Cambridge, Mass. On the paternal side he was descended from a Scotch-Irish family who emigrated to this country in the early part of the last century. His grandfather, Moses Wiley Gray, was born at Worcester, Mass., December 31, 1745, and was married in 1769 to Sallie Miller. He went in 1787 to Vermont, where his wife soon afterwards died; and when their son Moses, the father of Asa Gray, was eight years old, the father and son moved still farther west, to Sauquoit Valley, then almost a frontier settlement. Sixteen years later, Moses Gray was married to Roxana Howard, a daughter of Joseph Howard, of English descent, who, leaving his home in Massachusetts, had settled in Sauquoit Valley the same year as the Gray family. Of their family of eight children, five sons and three daughters, Asa was the first-born.

When a boy he assisted his father in the smaller duties connected with his farm and tannery; but at an early age he showed a much greater fondness for reading than for farm-work, and the father soon came to the conclusion that his son would make a better scholar than farmer. Until he was about twelve years old, the only education he received was what could be obtained for a part of the year in the small district school, and in the small private school at Sauquoit taught by the son of the parish pastor. He was then sent to the grammar school at Clinton, N. Y., where he remained for two years; and when, in the autumn of 1825, his teacher, Mr. Charles Avery, accepted a place in Fairfield Academy, young Gray followed his instructor to that place, where for four years he pursued elementary mathematical and classical studies. Connected with the Fairfield Academy was a Medical School which enjoyed a high reputation, and was attended by two hundred students, a large number for that time. Dr. James Hadley, the Professor of Materia Medica and Chemistry in the Medical School, also gave some instruction in the Academy, and it was probably through his influence that Gray's attention was first strongly drawn towards natural science. Apparently, he was not at first so much interested in plants as in minerals; and it was not until towards the close of his course in the Academy that his passion for plants was aroused by reading the article on Botany in the Edinburgh Encyclopædia, and his delight the following spring at being able to make out with the aid of Eaton's Manual the scientific name of the common Claytonia is now a well known story.

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Following his father's wish, which probably was in accord with his own inclination, he decided to study medicine, and formally entered the Fairfield Medical School in 1829, although for two years previously, while a student in the Academy, he had attended some of the medical lectures. The sessions of the Medical School, like those of the Academy, hardly occupied more than six months of the year, and the remainder of the time was spent in study with different physicians in the neighborhood of Sauquoit, one of whom, Dr. John F. Trowbridge of Bridgewater, was a man of good scientific attainments. He was thus in an excellent position for collecting, and even before he graduated he had brought together a considerable herbarium, and had entered into correspondence with Dr. Lewis C. Beck of Albany, and Dr. John Torrey of New York, who aided him in the determination of his plants. He received his Doctor's degree at Fairfield on February 1, 1831. never, however, entered upon the practice of medicine; but after receiving his degree he became instructor in chemistry, mineralogy, and botany in Bartlett's High School at Utica, N. Y., and taught those subjects, for a part of the year, from the autumn of 1831 to 1835.

The first actual record of any public lectures on botany given by him is found in a circular of the Fairfield Medical School, dated January, 1832, in which the following statement is made: "Asa Gray, M.D., will give a course of lectures and practical illustrations on botany, to commence [in June] and continue the same time with the lectures on chemistry [six weeks]. Fee, \$4.00." This course was attended apparently by ten persons; for he states that he spent the \$40 earned from these lectures in making a botanical excursion to Niagara Falls. It appears to be the case, however, that in the previous year, just after graduation, he had given a few lectures on botany in the Medical School, in the absence of the regular instructor, Dr. Beck; and a little later, he gave another course of lectures on mineralogy and botany at Hamilton College, Clinton. During other intermissions of his work at Bartlett's School, he made mineralogical and botanical excursions to different parts of New York and New Jersey; and it was while living at Utica that he published in the American Journal of Science of October, 1833, his first scientific paper on new mineral localities in Northern New York, written in connection with Dr. J. B. Crawe.

In the autumn of 1833, having leave of absence from Bartlett's School, he accepted the position of assistant to Professor John Torrey, in the chemical laboratory of the Medical School of New York. His time was here mainly occupied in botanical studies; and, besides aiding Dr. Torrey in his botanical work, he prepared and published several

original papers of his own, of which his memoir on *Rhynchospora* may be said to be his first contribution to descriptive botany. His connection with Bartlett's School ended early in 1835, and, although the financial condition of the New York Medical School did not permit his continuing as assistant of Dr. Torrey, he returned to New York in the autumn of 1835, and accepted the position of curator and librarian of the Lyceum of Natural History,—a position which gave him leisure for continuing his botanical studies, and to prepare his first text-book, "Elements of Botany," which appeared in 1836.

About this time a Government expedition, since known as the Wilkes Exploring Expedition, was fitting out, and the position of botanist of the expedition was offered to Dr. Gray in the summer of 1836. The expedition did not sail, however, until two years later; and meanwhile, wearied by the numerous delays and uncertainties about the management of the expedition, Dr. Gray resigned his position and settled in New York, where, in company with Dr. Torrey, he worked energetically on the preparation of the earlier parts of the "Flora," of which the first two parts appeared in October, 1838. While occupied in this work, a new State University had been founded in Michigan, and Dr. Gray accepted the chair of botany which was offered to him, with the understanding that he should be allowed to spend a year abroad in study before beginning his official duties.

The elaboration of the new "Flora" made it necessary for him to examine the types of American plants in foreign herbaria; and in November, 1838, he started on the journey which was not only to give him the means of clearing up much of the existing confusion with regard to the identity of previously described North American species, but, what was more important, was to bring him into close scientific and social relations with the botanical lights of a generation now long past, and with those who were then the young men of promise, a brilliant group, of which Sir J. D. Hooker and A. De Candolle are now almost the only survivors.

He returned to America in November, 1839, but never assumed the duties of Professor at Michigan. He was absorbed in his work on the "Flora," and, refreshed and stimulated by what he had seen and heard abroad, he was pushing rapidly ahead with the second volume, of which he wrote the greater portion, and at the same time printing a "Botanical Text-Book," which was to form the basis of his many subsequent text-books, when he was invited to Cambridge to fill the newly endowed chair of the Fisher Professorship of Natural History in Harvard College.

He accepted, and in 1842 took up his residence in Cambridge. second volume of the "Flora" was completed the following year. was at once favorably received in learned and social circles of Cambridge and Boston; and when delivering a course of lectures at the Lowell Institute, he first became acquainted with Miss Jane Lathrop Loring, daughter of Mr. Charles Greely Loring of Boston, to whom he was married on May 4, 1848. From this time his energies were devoted to building up a botanical establishment at Cambridge, - for what was in existence before 1842 hardly deserves mention, - and to the completion of a "Flora of North America." The number of collectors and explorers had by this time greatly increased; and the material they had brought together contained so much that was new, that it was plain that the original plan of the "Flora" must be changed, for the two volumes already published had hardly appeared when a revision seemed necessary. It was not until many years later, in 1878, that the first part of the new "Flora" appeared; and he continued to labor toward the completion of his great work until death forced him to relinquish the unfinished task.

He continued in the exercise of the active duties of lecturer and instructor until 1872, when he was relieved of this charge by the appointment of a colleague, Prof. G. L. Goodale; but he gave occasional lectures in the College for a few years longer. In 1873 he resigned his office of Director of the Botanic Garden, and Prof. C. S. Sargent was appointed his successor. He retained the title of Fisher Professor and Director of the Herbarium until his death, although he was in part relieved of the responsibilities of the latter position by the appointment of Mr. Sereno Watson as Curator of the Herbarium in 1874.

His long residence and arduous labors at Cambridge were varied and relieved by several journeys, some of which were of considerable extent, and all of which were made to contribute to the advancement of work on the "Flora," either by enabling him to examine in the field the plants which he was studying, or by examination of foreign herbaria, and consultations with leading foreign botanists. He made three trips to California, in 1872, in 1877, when he was in company with Sir J. D. Hooker, and in 1885, when he visited not only Southern California and the great Colorado Cañon, but journeyed into Mexico as far as Orizaba and Cordoba. He was once in Florida, in 1875, and made, besides, several trips to the mountains of North Carolina, where he botanized at different times with his botanical friends, Sullivant, Carey, Engelmann, Canby, and Redfield.

He made in all six journeys to Europe, including the journey

already mentioned and a short business trip of six weeks to Paris in the summer of 1855. On the other journeys he was accompanied by Mrs. Gray. When abroad, he always spent much of his time with the English botanists, among whom he counted many warm personal friends: and he looked forward with special pleasure to his visits at Kew, where he was welcomed by the Director, Sir W. J. Hooker, and by his son and successor, Sir J. D. Hooker, for forty years his intimate friend, whose opinion in botanical matters he esteemed more highly than that of any of his contemporaries. In his second journey, from June, 1850, to August, 1851, he travelled through France, Germany, and Holland, and spent two months with Bentham at his home in Herefordshire, studying the plants of the Wilkes Expedition, upon which he was then working. The fourth journey, from September, 1868, to November, 1869, was undertaken at a time when he was much overworked, and he spent the winter in Egypt, that country being almost the only spot where there was nothing to tempt him to botanize, besides visiting Italy, France, Germany, and England. event of the journey of September, 1880, to November, 1881, was a trip to Spain, a country where he obtained much relief from botany.

His last journey, on which he started in 1887, was a triumphant farewell, in which were heaped upon him the honors bestowed on few He visited friends in France, Austria, and Germany; stopped at Geneva to see De Candolle, his life-long friend, older by four years than himself, and sorrowfully bade him what both must have felt to be a last farewell; then hurried back from the Continent to receive the Doctor's degree from the three great British Universities, and to attend the meeting of the British Association at Manchester. Here he saw many old friends, and met for the first time three of Germany's most distinguished botanists, - Cohn, Pringsheim, and the lamented De Bary, whose untimely death was to come but a few days before his own. At Manchester he was brought into contact with a large number of young botanists, who were charmed with his genial manner, and astonished at his well preserved vigor of body, as well as mind. He returned to America in October, apparently in perfect health, and resumed active labor on the "Flora"; but while busied with the preparation of the Vitaceæ for that work, he was suddenly stricken with paralysis, on the morning of November 28, and lingered in a partially conscious condition until the evening of January 30, when he passed calmly away.

By the death of Asa Gray, this Academy has lost a member whose activity and zeal were unceasing, and whose brilliant talents as a scien-



tific writer, not surpassed by those of any of the illustrious names on our roll, added much to the reputation of the society at home and abroad. Elected a Corresponding Member in 1841, he became an active member in 1842, on his settlement in Cambridge, and served as Corresponding Secretary from 1844 to 1850, and again from 1852 to 1863, and as President from 1863 to 1873. During this long membership of more than forty years, his attendance was always exemplary. The storms of winter and the inclemencies of spring, which kept younger men at home, did not prevent his coming from the remote Botanic Garden regularly to attend the meetings. Although an honorary member of most of the learned societies of this country, and of many of the most prominent societies of Europe, including the Royal Society of London, the French Academy, and the Imperial Academy of St. Petersburg, of which he was one of the very few Americans who have been elected corresponding members, this Academy was the society in which he felt the greatest interest, and was most at home.

There are few volumes of our Proceedings which do not contain important communications from his pen. One of the earliest of his works, the "Chloris Boreali-Americana," was printed in the third volume of the Academy's Memoirs, in 1846; and to subsequent volumes he contributed "Plantæ Fendlerianæ Novi-Mexicanæ," presented in November, 1848; "Plantæ Novæ Thurberianæ," and "Note on the Affinities of the Genus Vavæa, Benth., also of Rhytidandra, Gray," August and October, 1854; and a group of four papers, entitled "Botanical Memoirs," in 1859, including one "On the Botany of Japan, and its Relations to that of North America," — a remarkable essay on the geographical distribution of plants, which stamped the author as worthy to rank with the great botanists of the world. We need not enumerate his many papers which have appeared in the Proceedings of the Academy, for they alone would fill several volumes. It was his custom to embody the results of his preliminary studies on the North American flora in the form of notes on critical species, descriptions of novelties, and monographs of genera, and sometimes orders, of which by far the greater part first appeared in our Proceedings, usually under the heading of "Botanical Contributions,"a long and very valuable series, dating from the paper "On some New Compositæ from Texas," presented December 1, 1846, and ending with the posthumous "Notes upon some Polypetalous Genera and Orders," presented April 19, 1888. Nor should we forget the many biographical notices in which he commemorated the lives and works of others with an appreciating discrimination, written in a manner peculiarly his own.

The botanical department of Harvard University was practically created by Asa Gray. In 1805 a small Botanic Garden was established at Cambridge, under the auspices and by the aid of the Massachusetts Society for Promoting Agriculture, and William Dandridge Peck was appointed Director and Professor of Botany. In 1818 he printed a "Catalogue of American and Foreign Plants cultivated in the Botanic Garden. Cambridge," in which 1,309 species were enumerated; but the list included some common cryptogams found everywhere, and a large number of phænogamic shrubs and weeds, common natives of the region. hardly to be counted as legitimate members of a botanic garden. Professor Peck died in 1822, when, owing to the low state of the funds, a Professor was not appointed; but Thomas Nuttall, the well known botanist and ornithologist, was appointed Curator of the Garden, and, later, Lecturer on Botany. This amiable but very reticent naturalist who apparently did not find his residence in Cambridge very congenial, for he describes himself as vegetating like his plants - resigned his position in 1833, and returned to Philadelphia. The Garden, such as it was, was then put under the charge of William Carter, a gardener, and the lectures on botany were given by T. W. Harris, the well known entomologist and Librarian of the College, and Dr. A. A. Gould of Boston. Not long before 1842 the directorship of the Garden was offered to Mr. George B. Emerson of Boston, who declined the position soon afterwards accepted by Dr. Gray in connection with the Fisher Professorship.

On Dr. Gray's accession there was no herbarium, no library, only one insignificant greenhouse, and a garden all in confusion, with few plants of value. In 1844 he moved into the house which had been built for Professor Peck in the Garden, and with his characteristic energy he soon brought together an herbarium and library, and arranged the Garden systematically. At the time of his marriage a small wing was added to the house, of which the lower story served as a study and herbarium until 1864. But the plants soon overran the limits of the herbarium, and finally the whole house was crammed with plants, - plants in the dining-room, in the attic, in the closets. and in the bedrooms; for whatever he could spare from a salary of \$1,000 at first, and \$1,600 afterwards, was spent on his herbarium and library. In 1864, dreading the danger from fire to a collection kept in a wooden house, he offered to present his collections to the College, on condition that a suitable building should be erected for their reception. Through the liberality of Mr. Nathaniel Thayer of Boston, a brick building to be used as an herbarium and library was

erected in 1864, at a cost of \$12,000; and, mainly through the agency of Mr. G. B. Emerson, a further sum of \$10,000 was raised, the income of which was to be used in defraying the current expenses of the Herbarium. From a letter by Dr. Gray to the President of the University, dated November 20, 1864, and a notice in the American Journal of Science of March, 1865, we learn that the Herbarium then contained at least 200,000 specimens, and the library about 2,200 botanical works, not including a good many pamphlets. There was also a set of 335 very costly illustrated works, contributed by Mr. John A. Lowell.

Since 1864 the Herbarium has been constantly enlarged, principally by exchanges, of which those from the Kew Herbarium especially were of very great value; so that it is now probably twice as large as in 1864, and forms practically a National Herbarium, for it is by far the largest and most valuable herbarium in America, and is excelled in size by but few of the older and richer herbaria of Europe, as those at Kew, Paris, Berlin, the De Candolle Herbarium at Geneva, and possibly that at St. Petersburg. In the representation of the Phænogams of North America outside the tropics, it is probably unequalled by any herbarium except that at Kew. The library at the time of Professor Gray's death was roughly estimated to contain something over 5,000 volumes and 3,000 pamphlets, but these figures are probably too low. Many of the additions since 1864 are the gift of Dr. Gray. In building up this vast collection, he gave not only much of his time and thought, but also an actual sum of money, which comes well up in the thousands, and, to crown all, manifested his devotion to the welfare and perpetuation of the collection by bequeathing to the University for its support the royalties on his publications.

The Garden during his administration was improved by the addition of several greenhouses, in which were cultivated a choice selection of exotics, and the rather limited space of the Garden itself was filled with good representatives of the flora of the temperate regions, the collection of Compositæ being especially important. In the absence of a sufficient endowment, activity on the part of the Director had to replace the want of money, and he, utilizing the means at hand, succeeded in making the Garden an exceedingly important means of exchange between foreign establishments and our own botanists and collectors. European botanists who visited the Garden wondered how, from such a small and ill-endowed establishment, so much had been done in aid of other institutions. The explanation lay in the skill and energy of Dr. Gray himself.

Grav's work as a teacher extended over a period of more than fifty years, dating from the first lectures on botany at the Fairfield Medical School, in 1831 and 1832, and the publication of his "Elements of Botany," in 1836. During that period he trained up a whole race of botanists, now scattered through all parts of the United States, so that wherever he went he was greeted by those who remembered his instruc-When at Santa Barbara in 1885, an elderly man, tion with pleasure. who seemed to be about his own age, introduced himself as a former pupil in his first class at Harvard. As a college lecturer he was not seen at his best, for his somewhat hesitating manner when he spoke extemporaneously was unfavorably contrasted with the fervid, almost impetuous utterance of Agassiz, and the clear exposition and dignified address of Jeffries Wyman, his two great contemporaries at Harvard. In his public addresses he always spoke from notes, and, especially in his later years, his strikingly expressive face commanded the attention of his hearers from the start. In the class-room he was personally much liked, and he made a strong impression on the majority of students, although, in the days when every student was forced to study botany, there were of course some who would not have cared for the subject under any cir-The instruction, as was natural, bearing in mind his own early training and the state of botany in this country at the time when he became Professor at Harvard, was confined mainly to the morphological study of flowering plants; for he recognized that, until some advance had been made in that direction, it was out of the question dealing adequately with the more technically complicated subjects of histology, embryology, and physiology.

For the instruction which he was obliged to give, the resources of the Garden and Herbarium and the ordinary college lecture-rooms at first sufficed, but at last it became necessary to provide a special laboratory and lecture-room at the Garden. A liberal friend of Dr. Gray and the College presented a sum of money for this purpose, and in 1872 a wing was added to the Herbarium. About this time the demand for laboratory instruction and equipment increased rapidly, and the new lecture-room and laboratory were soon found to be inadequate to meet the needs of the increasing calls for microscopic and physiological work, and they were at length abandoned. It is not surprising that Dr. Gray could not foresee how great the growth in this direction was to be, even in his own life. Probably no person of his age could have foreseen it.

His Herbarium was, at one period or another, the resort of nearly all the active working botanists of the country, and thither came many

young men who were afterwards to aid in the development of botanical studies in the United States. His intercourse with them was always free and unrestrained by formalities of any kind, and he seemed more like a learned friend than a teacher. Passing to and fro from his own study to the Herbarium, he greeted all cordially, watching and criticising sharply but good-naturedly the work that was going on. No one enjoved a hearty laugh more than he, and every now and then he would brighten the work by some anecdote from the large stock which his retentive memory ever had at hand; always, however, for the purpose of emphasizing some point, or illustrating some fact which he wished to bring out more clearly, but never allowing the attention of those about him to be distracted from their work. Life at the Herbarium was indeed a pleasure, and the more serious work was well seasoned and spiced in the days when the agile assistant, Charles Wright, skipped about like a squirrel, his diminutive body in Cambridge, his larger mind wandering away in his beloved Cuba and the Pacific Islands, - when Brewer, less continent than his teacher in the matter of anecdote, saw in every plant before him some episode of his own life in camp. The approach of Dr. Gray, heralded by his cheery laugh, or perhaps by a mild anathema against the gardener, who every morning, regardless of the intentions of nature, deluged the Cacti placed in the corridor, we all understood to mean business, for, if joking was allowed, trifling was not. We learned something about botanists as well as about botany, and often wondered whether Robert Brown were really as great as he was represented; and, on the rare occasions of a visit from a man like Dr. Torrey or Dr. Engelmann, we asked ourselves whether there was any chance that the younger generation of botanists would bear any comparison with the older. None who have worked under Dr. Gray at the Herbarium will forget the deep personal interest he always manifested in their work and future prospects. He always encouraged and stimulated without holding out false hopes. To those who wished to devote themselves to botany in the years still recent, when it was scarcely possible for a botanist to live by botany alone, he used to say: "Study medicine, and if you then still want to be a botanist, go ahead. Your medicine will keep your botany from starving."

Great as was the direct influence of Dr. Gray upon the students with whom he came in contact, his influence on the development of botany in this country through the medium of his numerous text-books and manuals was even more important. His first text-book, "Elements of Botany," written when he was only twenty-six years old, shows many of the best characteristics of his later works, being written in a smooth,

graceful style, with the different topics clearly and methodically arranged. The vigorous defence of the natural system of classification, which now appears superfluous, indicates that the author of 1836 was a progressive young man, who had shaken off the conservatism which prevailed among American botanists of that period. That he was young and inexperienced is occasionally shown, as in the amusing statement that "the herbarium of a diligent botanist will pass so frequently under his observation that any very extensive ravages [by insects] can hardly take place without his being aware of it in time to check the progress of the destroyers." He evidently had no conception of how large his own collection would become in a few years.

The "Elements" of 1836 developed into the "Botanical Text-Book" of 1842, in which the portion relating to systematic botany was much more fully treated than in the earlier volume. The later editions, which appeared at intervals until 1879, are familiar to every one, for they have been the means of opening the world of botany to more than one generation of American botanists. In 1868 the "Lehrbuch der Botanik," by Sachs, appeared. That work was a genuine revelation, showing the advance which had been made by experts in the science of botany, and, although somewhat above the capacity of the common student, it was destined to produce in a few years a revolution in the method of botanical instruction.

Recognizing the new era which had opened in botany, Dr. Gray revised the plan of the "Text-Book," with a view of bringing it into accord with the more widely developed science of the day, and in 1879 issued the first volume of the revised work, in which he included the Morphology of Phænogams, Taxonomy, and Phytography, thus covering the greater part of the ground of the original "Text-Book," intrusting to his colleague, Professor Goodale, the volume on Physiological Botany, which appeared in 1885 as worthy companion of its predecessor, and to the writer the volume on Cryptogams. He hoped, but hardly could have expected, to write a fourth volume, on the Orders of Phænogamous Plants. It is deeply to be regretted that he was never able to write this volume, for it would have enabled him to present the general views on classification derived from a long and exceptionally rich experience. No better text-book on the subject had ever been written in the English language than Gray's "Text-book" in the original form; and, although botanical instruction is now very different from what it used to be, it is still true that, as an introduction to the study of Phænogams, the group to which beginners naturally turn their attention, the later "Structural Botany" is likely to hold its own for some time to come. In 1887, just before he started on his last European journey, he finished a small book giving in an abbreviated form the substance of the Structural Botany, as well as some chapters on Cryptogams; and for this his latest text-book he revived the title of his earliest work, "Elements of Botany."

The "Manual of the Botany of the Northern United States," of which the first edition appeared in 1847, needs no words of praise here. There are probably few members of the Academy who do not own, or have not at some time owned, a copy of this model work. Occasionally some over-wise person has discovered that certain plants grow a few inches taller or bloom a few days earlier than is stated in the "Manual"; but the botanist is yet to be born who could write a more clear, accurate, and compact account of the flora of any country. The only regret is that he could not have written manuals for all parts of the country.

Dr. Gray had the rare faculty of being able to adapt himself to all classes of readers. With the scientific he was learned, to the student he was instructive and suggestive, and he charmed the general reader by the graceful beauty of his style, while to children he was simplicity itself. The little books, "How Plants Grow," and "How Plants Behave," found their way where botany as botany could not have gained an entrance, and they set in motion a current which moved in the general direction of a higher science with a force which can hardly be esti-His scientific friends, especially those abroad, sometimes blamed him for spending time in popular writing; but he may have understood himself and his surroundings better than they. botany was a pleasure, as well as a business. Few wrote as easily as he, and, so long as he spent most of his time in higher work, he certainly had a right to amuse himself with writings of a popular character if he As it was, he interested a multitude of readers in the subjects which he had at heart, and if he was not permitted to live to see the completion of his greatest work, "The Synoptical Flora," he at least was able to leave the work at a point where it could be continued by a trusted friend, in sympathy with all his plans.

As a reviewer he was certainly extraordinary. Some of his reviews were, in reality, elaborate essays, in which, taking the work of another as a text, he presented his own views on important topics in a masterly manner. Others were technically critical, while some were simply concise and very clear summaries of lengthy works. Taken collectively, they show better than any other of his writings the literary excellence

of his style, as well as his great fertility and his fairness and acuteness as a critic. Never unfair, never ill-natured, his sharp criticism, like the surgeon's knife, aimed not to wound, but to cure; and if he sometimes felt it his duty to be severe, he never failed to praise what was worthy. The number of his reviews and notices written during his connection with the American Journal of Science as editor and assistant editor for over thirty years, and for the North American Review, the Nation, the Atlantic Monthly, and numerous other journals, is enormous, and it almost seems as if he must have written notices of the greater part of all the botanical works he had ever read. Those intimately acquainted with him more than half believed that he was able to write good notices of books written in languages which he could not read. He was able, as if by instinct, to catch the spirit and essence of what he read, without any exertion on his part. One who wrote so much might have become monotonous. But he was never prosy, and his style was so easy and flowing, and so constantly enlivened by sprightly allusions and pleasing metaphors, that one could read what he wrote for the mere pleasure of the reading. His was one of the rare cases where Science had appropriated to herself one who would have been an ornament to any purely literary profession.

It would be presumption were we to express an opinion on the position of Gray as a scientific botanist. Fortunately for us, it is unnecessary. The greatest living systematic botanist, Sir J. D. Hooker, the one by his attainments and position fitted above all others to speak with authority on the subject, has already recorded his opinion in the following words:—

"When the history of the progress of botany during the nineteenth century shall be written, two names will hold high positions: those of Professor Augustin Pyrame De Candolle and of Professor Asa Gray. . . . Each devoted half a century of unremitting labour to the investigation and description of the plants of continental areas, and they founded herbaria and libraries, each in his own country, which have become permanent and quasi-national institutions. . . . There is much in their lives and works that recalls the career of Linnæus, of whom they were worthy disciples, in the comprehensiveness of their labour, the excellence of their methods, their judicious conception of the limits of genera and species, the terseness and accuracy of their descriptions, and the clearness of their scientific language."

The accuracy of the resemblance of Gray and De Candolle, so admirably and justly expressed by Hooker, will be recognized by all botanists.

Gray was the De Candolle of America, whose mission it was to bring together the scattered and crude works of the earlier explorers and botanists and the vast unwrought material of his own day, and to combine them with his surpassing skill into one grand comprehensive work which should fitly describe the flora of a continent. But while recognizing the resemblance between De Candolle and Gray in their mode of work and the purpose for which they strove, we can only marvel how it was possible for a poor farmer's boy in America, without a university education, to become the peer of one of Europe's best trained botanists.

From his training and early surroundings we might have expected him to be energetic and original, but we should not have expected to find him highly polished and cultured. His associates at Fairfield and Clinton were persons of scientific tastes, and, even if their attainments were not of the highest quality, they encouraged his fondness for natural history. But it is not easy to see how he obtained the literary training which enabled him to write with the ease and elegance found even in his earlier works, for although a man may by nature be a good observer of natural objects, a finished style comes only with training and experience. From his teacher, Avery, he could not have received much in the way of training; for Dr. Gray himself says that he did not give him the sharp drilling and testing which was needed. His residence with the Torrey family in New York first placed him in a society where literary excellence as well as scientific knowledge was prized; and while he profited by the accuracy and strict scientific methods of Dr. Torrey, then the foremost American botanist, the frequent conversations and kindly criticisms of Mrs. Torrey made good many of the literary deficiencies of his early training. He was also aided while in New York by the criticisms and suggestions made on some of his earlier manuscripts by the cultured botanist, Mr. John Carey. But he must have been an apt pupil, for, while still with Dr. Torrey, he showed that in point of clearness and accuracy he was not much inferior to his highly respected teacher, and in the second volume of the "Flora" he proved himself to be quite his equal.

The plan of the "Flora of North America" originated with Dr. Torrey; but when his pupil went to Cambridge to assume the duties of his new position, neither of them suspected the magnitude of the task which they had undertaken, nor the modifications which the plan must ultimately undergo. The pupil was now in a more fortunate position than his teacher, for Gray was henceforth able to devote himself to his favorite science, while Dr. Torrey could only employ his leisure hours

in botany. The two volumes of the original Torrey and Gray "Flora" will always remain a memorial of the unbroken friendship of America's two greatest botanists, alike in the spirit which animated their work and in the reverent simplicity of their characters.

The greater part of Gray's scientific work during the thirty-five years following the completion of the second volume of Torrev and Grav's "Flora," in 1843, had a more or less direct bearing on the contemplated revision and enlargement of that work. Besides the papers printed in the Academy's publications, he wrote a very large number of monographs and notes on points connected with the determination and description of new and doubtful species. They are scattered through the proceedings of different learned societies, and the columns of the American Journal of Science, the Torrey Bulletin, Botanical Gazette, the Naturalist, and other American, as well as European journals. One of his most important works was "Genera Floræ Americæ Boreali-Orientalis Illustrata" (1848-49), in which he intended to figure and describe all the genera of the Eastern States, with the aid of the artist, Mr. Isaac Sprague. Of this work only two of the proposed volumes were ever published, owing to the expense entailed. Other important papers were "Plantæ Wrightianæ Texano-Neo-Mexicanæ," in the Smithsonian Contributions of 1852 and 1853; "Plantæ Lindheimerianæ," written in connection with Dr. Engelmann; "Reports on the Botany of the 32d, 38th, 39th, and 41st Parallel Expeditions," in connection with Dr. Torrey; Gamopetalæ in Watson's Flora of California, etc. An examination of the complete list of his works, which will soon be printed in the American Journal of Science, would alone convey any adequate idea of his extraordinary fertility as a writer, and the wide range of his investigations.

After this long preparation of thirty-five years, the first part of the "Synoptical Flora," including the Gamopetalæ after Compositæ, appeared, in 1878. It formed the first part of the second volume; for, on the revised plan, the first volume was to include the Polypetalæ and Gamopetalæ through Compositæ, and the second volume the remaining Exogens and the Endogens. A second part, including from Caprifoliaceæ through Compositæ, appeared in 1884, and in 1886 supplements to both parts were issued, and the whole bound in one volume. He was at work on the Polypetalæ, and had nearly finished the Vitaceæ, when attacked by his last illness, and the unfinished volumes must now be completed by him who was his associate for many years, and, after Dr. Gray himself, the best fitted for the work.

Gray's critical knowledge of the Flora of North America not only

placed him at the head of all American botanists, but also gave him a high reputation abroad. In his knowledge of the difficult order Compositæ, the largest of all the orders of flowering plants, and the one in which he always felt the most interest, he probably surpassed any living botanist. He was at one time urged by Bentham and Hooker to treat that order in their classic "Genera Plantarum," but, as the work involved a residence at Kew for a considerable time, he was obliged to decline the offer.

It was, however, more especially through his observations on the geographical distribution of plants made incidentally during the progress of his work on our own flora, that he was recognized as a naturalist of the highest type by the scientific circles of Europe. When we consider the marked capacity for studies of this nature which he afterwards exhibited, remembering the brilliant contributions to Plant Geography which resulted from the explorations of Robert Brown, Darwin, and Hooker, we can only regret that Gray did not sail as botanist of the Wilkes Expedition. The collectors of the expedition, Dr. Charles Pickering, W. D. Brackenridge, and William Rich, brought back many interesting plants, of which the Phænogams, excepting those from the Pacific Coast of America sent to Dr. Torrey, were placed in his hands for description. But Gray would have been more than a collector. He would have brought back impressions, and, recalling the charming narrative of the illustrious naturalist of the Beagle, we can imagine the pleasure with which we should have read the journal of a botanist, written with the delicate humor and the keen appreciation of the beautiful and curious in nature which Asa Gray possessed.

The study of the Wilkes plants, in which he was aided by Bentham's large experience, gracefully acknowledged in his Memorial of Bentham in the American Journal of Science of February, 1885, introduced him to an exotic flora of large range. The work appeared in 1854 as a quarto volume of nearly eight hundred pages, with an atlas of a hundred folio plates.

His first \* paper on the distribution of plants appeared in the American Journal of Science of September, 1856, and was followed by two other parts the next year. It bore the title of "Statistics of the Flora of the Northern United States," and was prepared at the time he was at

<sup>\*</sup> In the paper "On the Botany of Japan," p. 442, Gray speaks of a paper on the distribution of plants in the American Journal of Science of an earlier date than the one here mentioned, but the writer is unable to identify the paper in question.

work on a second edition of the "Manual," partly in response to a request from Darwin for a list of American alpine plants. In this paper he gave a general view of the characteristics of the North American flora, with tables of species showing the extension of alpine plants, and the comparative distribution of Eastern and Western species, and their relation to species of Europe and Asia, although he states that he must defer making an extended comparison with the plants of Northeastern Asia until he has studied some recent collections from the northern part of Japan. The most important conclusions reached in this paper may be stated in his own words: "All our strictly subalpine species (with two exceptions) which are common to us and to Europe, extend northward along the central region of the continent quite to the arctic sea-coast. While curiously enough, eleven, or one third of our strictly alpine species common to Europe, - all but one of them arctic in the Old World, - are not known to cross the arctic circle on this continent. This, however, might perhaps have been expected, as it seems almost certain that the interchange of alpine species between us and Europe must have taken place in the direction of Newfoundland, Labrador, and Greenland, rather than through the polar regions." Again: "The special resemblance of our flora to that of Europe, it is clear, is not owing simply either to the large proportion of genera in common, or to anything striking or important in the few genera nearly or quite peculiar to the two. The latter, indeed, are insignificant in our flora, and not to be compared, as to any features they impart, with the much more numerous and really characteristic genera which are shared by the Eastern United States and Eastern temperate Asia. We must look for it in the species, partly in the identical ones, and partly in those which closely answer to each other in the two floras." He accounts for such cases as the occurrence of Phryma Leptostachya in the United States and Nepal as follows: "We should therefore look in one and the same direction for the explanation of these extraordinary no less than of the more ordinary cases of distribution, and . . . should refer such anomalous distribution to very ancient dispersion."

The plants from Japan to which he referred were collected by Charles Wright, botanist of the North Pacific Exploring Expedition, known as the Ringgold and Rodgers Expedition, of which Dr. Gray gave an account in a paper "On the Botany of Japan, and its Relations to that of North America, and of other Parts of the Northern Temperate Zone," presented to this Academy, December 14, 1858, and January 11, 1859, and published, April 25, 1859, in the sixth volume of the Memoirs. This memoir raised his reputation to its highest point vol. xxIII. (x. s. xv.)

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among scientific men, and, appealing again to the authority of Sir J. D. Hooker, "in point of originality and far-reaching results was its author's opus magnum." In referring to his previous paper in the American Journal, he states with great candor, that, from the facts there brought out. - "1. that a large percentage of our extra-European types are shared with Eastern Asia; and 2. that no small part of them are unknown in Western North America," - Mr. Bentham was the first to state the natural conclusion that the interchange between the temperate floras even of the western part of the Old World and of the New, has mainly taken place via Asia. He cites Bentham's suggestion of a continuity of territory between America and Asia, "under a latitude, or at any rate with a climate, more meridional than would be effected by a junction through the chains of the Aleutian and the Kurile Islands." He then proceeds to show why a connection in a more meridional latitude need not be assumed; and, fortified by the wide geological knowledge of his friend, Prof. J. D. Dana, he gives a masterly account of the relations of the floras of the North Temperate regions from the Cretaceous period to the present time, accounting for the present distribution by migrations of species from the Arctic regions due principally to the different climatic conditions of the pre-glacial, glacial, and post-glacial eras. The relations of the floras of Eastern America and Eastern Asia was a favorite topic with him, and he often spoke on the subject in public; his two most important addresses in which he referred to plant distribution being that on "Sequoia and its History," delivered as retiring President of the American Association for the Advancement of Science in 1872, and a lecture on "Forest Geography and Archæology," read before the Harvard Natural History Society in 1878, and afterwards translated in the Annales des Sciences.

The study of plant distribution necessarily involved the question of the origin of species, and this brings us to a consideration of the relations of Gray to Darwin and Darwinism. Gray first met Darwin at Westbank, the residence of Sir W. J. Hooker at Kew, in 1851; and their correspondence dates from a letter of Darwin written April 25, 1855, asking for information about the alpine plants of the United States. How intimate and frequent their correspondence became, and how deeply each was interested in the work of the other is admirably shown in the "Life and Letters of Charles Darwin." The published letters present a vivid picture of the inner scientific life of these two men, — both equally simple, earnest, remarkably free from prejudice, and

anxious to do justice to the work of others. Many of the problems upon which Darwin was at work were those in which Gray was most interested; and he was often able to aid Darwin by his observations, and still more by his judicious and always acceptable criticisms. While the naturalist at Down was absorbed in the study of climbing plants and cross-fertilization, the greenhouses at Cambridge were also used as nurseries for the growth of climbers, and the odd, irregularly flowered plants which ought to be cross-fertilized. The writer recalls the time when Dr. Gray hardly ever passed in or out of the Herbarium without stroking — patting on the back by way of encouraging them it almost seemed — the tendrils of the climbers on the walls and porch; and when, on the announcement that a student had discovered another new case of cross-fertilization in the Garden, he would rush out bareheaded and breathless, like a schoolboy, to see the thing with his own critical eyes.

Darwin, in a letter dated July 20, 1856, confided to Gray that he had "come to the heterodox conclusion that there are no such things as independently created species, — that species are only strongly defined varieties." In this letter he also says, "I assume that species arise like our domestic varieties with much extinction." About a year after this, September 5, 1857, Darwin wrote to Gray the now famous letter, in which he propounded the law of the evolution of species by means of natural selection; and it was this letter, read at the Linnean Society, July 1, 1858, on the occasion of the presentation of the joint paper of Darwin and Wallace, "On the Tendency of Species to form Varieties; and on the Perpetuation of Varieties and Species by Natural Means of Selection," which fixed the date of the priority of the great discovery as due to Darwin. What were Gray's own views on the subject of evolution previous to the publication of the "Origin of Species," in November, 1859, may perhaps be inferred from some remarks which he made on January 11, 1859, when he presented his paper "On the Botany of Japan" to this Academy. He then stated that "the idea of the descent of all similar or conspecific individuals from a common stock is so natural, and so inevitably suggested by common observation, that it must needs be first tried upon the problem [of distribution], and if the trial be satisfactory, its adoption would follow as a matter of course." In brief, he was inclined to accept evolution, but wished more proof; and nearly three years earlier, in a letter to Professor Dana, written December 13, 1856, he had well expressed his own attitude by saying, "I have as yet no opinion whatever, and no very strong bias." He saw what was coming, however, and in a later letter to Professor Dana, anticipating the publication of the "Origin of Species," he says, "You may be sure

that before long there must be one more resurrection of the development theory in a new form, obviating many of the arguments against it, and presenting a more respectable and more formidable appearance than it ever has before."

Gray was one of the favored three, including Hooker and Lyell. to whom Darwin sent advance sheets of the "Origin of Species" prior to its publication in November, 1859; and of his review in the American Journal of Science of the following March, Darwin wrote. "Your review seems to me admirable, - by far the best I have read." The review certainly presents most accurately, succinctly, and attractively Darwin's own views; but Gray does not even here announce that he is himself a complete convert to the doctrine, as is seen by the following citation: "What would happen if the derivation of species were to be substantiated, either as a true physical theory, or as a sufficient hypothesis? The inquiry is a pertinent one just now. For, of those who agree with us in thinking that Darwin has not established his theory of derivation, many will admit with us that he has rendered a theory of derivation much less improbable than before; that such a theory chimes in with the established doctrines of physical science, and is not unlikely to be largely accepted long before it can be proved." And the similar statement in the Atlantic Monthly of October, 1860: "Those, if any there be, who regard the derivative hypothesis as satisfactorily proved, must have loose notions of what proof is. Those who imagine it can be easily refuted and cast aside must, we think, have imperfect or very prejudiced conceptions of the facts concerned and of the questions at issue."

In 1876 he brought together in a volume, entitled "Darwiniana," his principal essays and reviews pertaining to Darwinism, taken from the American Journal of Science, the Nation, and the Atlantic Monthly, and added a chapter on "Evolutionary Teleology"; and in 1880 he published "Natural Science and Religion," two lectures delivered to the Theological School of Yale College, before a critical audience, who listened with the deepest interest to what was, in some points, his most advanced view of natural selection. We need not dwell on a subject about which so much has lately been written by far abler pens than ours. Briefly stated, Gray was probably the best expounder of Darwinian principles, — meaning thereby those actually advocated by Darwin himself, and excluding the wild deductions attached to the original theory by those who deserve the name of Darwinissimists rather than Darwinists, — although he himself regarded natural selection as a less efficient cause than it was assumed to be by Darwin.

His influence as an exponent of Darwinism was due partly to the admirable clearness and candor of his reviews, and his interesting way of putting things; for his fertile imagination was constantly discovering apt similes to illustrate otherwise dry arguments. It was also due in part to his known caution and conservatism, and his professed Christian faith. If an avowed accepter "of the creed commonly called the Nicene" saw nothing in Darwinism which implied atheism, or was opposed to the idea of design on the part of the Creator, surely one might, at least, listen to his account of the development theory with safety. To his hearers at New Haven, in 1880, he said: "Natural selection by itself is not an hypothesis, nor even a theory. It is a truth, — a catena of facts and direct inferences from facts. . . . There is no doubt that natural selection operates; the open question is, what do its operations amount to. The hypothesis based on this principle is, that the struggle for life and survival of only the fittest among individuals, all disposed to vary and no two exactly alike, will account for the diversification of the species and forms of vegetable and animal life, - will even account for the rise, in the course of countless ages, from simpler and lower to higher and more specialized living beings." He gave it as his opinion that natural selection is, on the whole, a good working hypothesis, but does not explain how wholly new parts are initiated, even if the new organs are developed little by little. He repeated over and over again in different reviews his belief that natural selection could not account for variation, and he stated the case particularly forcibly in his "Evolutionary Teleology": "Natural selection is not the wind which propels the vessel, but the rudder which, by friction, now on this side and now on that, shapes the course. The rudder acts while the vessel is in motion, effects nothing when it is at rest. Variation answers to the wind. . . . Its course is controlled by natural selection. This proceeds mainly through outward influences. But we are more and more convinced that variation . . . is not a product of, but a response to, the action of the environment. Variations are evidently not from without, but from within."

But how do variations arise? According to Gray, by virtue of some inherent power imparted in the beginning by Divine agency. That granted, natural selection would in great part account for the present condition and distribution of life, so that one could be a Darwinian and Deist at the same time. Gray further believed that variation is apt to follow in certain more or less regular directions, and particularly in beneficial directions. Here he differed very widely from Darwin. The one saw design where the other could not, and it must be confessed

that Gray was treading on delicate ground, scientifically if not theologically speaking, when he affirmed the direction of variation in beneficial lines. For what is meant by beneficial? Beneficial to whom? Beneficial for what purpose? In one sense, any variation which tends to enable a living being to survive in the struggle for existence is beneficial; and to say that any being or structure has survived is the same as saying that the variation from which it sprang was beneficial. But Gray apparently uses the word beneficial in the sense of being fore-ordained to be beneficial.

Perhaps we must look to inheritance itself for an explanation of the difference in the views of Gray and Darwin. The Gray family were devout members of the Presbyterian Church, and throughout his life Dr. Gray adhered faithfully to the orthodox faith of his fathers. his own views being in harmony with those of the liberal branch rather than with those of the conservative branch of that communion. The agnostic position of Darwin may perhaps be inferred from his own description of himself and his father as belonging "nominally to [the] Church of England," an expression which leads one to believe that he was hardly to be counted a member of that or any other denomination. When a young man, Gray certainly had no leanings towards evolution. In his review of the "Vestiges of Creation," in the North American Review of 1846, he wrote: "Although 'geology fully proves' that there have been various creations, that different species were created at different periods, and that some of the humblest and simplest first appeared, while land animals, quadrupeds, quadrumana, and bimana were not introduced until after the earth was fitted for their residence. yet we are still to be convinced that they were not then created as perfect as they now are." But he was convinced later, when he studied the relations of the North American flora to that of Asia, and he accepted without hesitation the view that the present species are not special creations, but derived from previously existing species at a time when the truth of the theory was scarcely recognized by any naturalists, and at a date when in the public mind a belief in evolution meant athe-He had the courage to avow openly his convictions, but, on the other hand, never allowed his convictions to be governed by wild speculations.

But we who have known Asa Gray so many years would now recall, not the great botanist, but rather the kind-hearted, genial man, whose sympathy cheered and whose wisdom guided, — whose heart was ever young, whose brain was ever active. His long life, unclouded by great

sorrow and almost free from personal enmities, was inspired throughout by a faith which never faltered. Retaining to the last the energy and vivacity of youth, his intellect broadening and ripening, his character growing more and more sweet and serene, he reminds us of one of those trees which bear flowers and fruit at the same time. Industrious to an extent that few could equal, his work done, he enjoyed society with a relish, and his ready wit, his inexhaustible stock of anecdotes, and his quick and keen appreciation of the best in literature and art, made him everywhere welcome. His own house was open to all, and even those who came to pay the simple tribute of staring were not often turned away. With a graceful hospitality to which wealth could have lent no greater charm, he entertained the learned of many nations, and welcomed with special cordiality his brother botanists, a long array, including not only the experts in the science, but the poor and struggling student as well. He shared with all the treasures of his knowledge, and, not infrequently, he added something from the modest competence which his industry had amassed. The words of good cheer from his lips were re-echoed in after years, and the life so honorable was not unhonored. If the numerous honorary degrees from learned societies at home and abroad testify to the esteem in which he was held as a scientific botanist, the warm congratulations of friends from all parts of the country when the memorial vase was presented on his seventy-fifth birthday show no less clearly how much he was beloved as a man. And when, during dreary weeks, his anxious friends hoped against hope, watching to catch the sound of the loved voice which would speak but could not, all felt that the message which he sought to utter must have been a benediction. But it was not needed. His life was a benediction, and, as his body was borne to its last resting place, the freshly fallen snow was not more pure than his character, nor the sparkling winter air more bright and clear than his intellect.

#### LAURENS PERSEUS HICKOCK.

LAURENS PERSEUS HICKOCK, D.D., LL.D., was born at Danbury, Connecticut, December 22, 1798, and died at Amherst, May 7, 1888. He graduated at Union College in 1820, then studied divinity, and served two short pastorates in his native State. In 1836 he became Professor of Theology in the Western Reserve College, Ohio. In 1844 he removed to Auburn, New York, to take a professorship in the Theological School. In 1852 he was elected to the Professorship of Mental and Moral Philosophy in Union College, and at the same



time was chosen Vice-President of that institution, Dr. Nott, the President, needing not infrequent aid in a charge which he had borne for nearly half a century.

In 1861, Dr. Hickock, as Acting President, assumed in full the duties of the office, and in 1867 was chosen as Dr. Nott's successor. In the following year he resigned the Presidency, and has since lived in retirement, wellnigh surviving the eminent reputation which he long bore as a teacher and an author. Thirty years ago his was probably the foremost name among the metaphysical writers in America. His several treatises on Psychology and Ethics manifest equally the most intimate conversance with the history of philosophy, and a rare capacity of original speculation and profound reasoning. Had his command of English style been commensurate with his learning and ability, his books would have won an enduring place among the master-works of his time. No man ever toiled through one of them without being doubly rewarded in the mental athleticism demanded for its perusal and in the wealth of thought to which he has found access; and men by far his inferiors have drawn from him much which, digested and assimilated, they have given to the world as their own. But deficiency in the arts of sentence-building and book-making has so limited the circulation of his works, that of the younger men of culture and science who have seen the notice of his death few know that in his special department he has left, if equals, no superior.

## MARK HOPKINS.

MARK HOPKINS, D. D., LL. D., was born at Stockbridge, February 4, 1802, and died at Williamstown, June 17, 1887. He graduated at Williams College in 1824, remained at the College as Tutor for two years, then studied medicine, and commenced the practice of his profession in New York in 1829. The following year he was recalled to Williams College as Professor of Rhetoric and Moral Philosophy, and became President in 1836, retaining during his presidency a large portion of his work as a teacher, and subsequently filling, in addition to his duty as President, the office of Professor of Christian Theology. Several years before his death he resigned the presidency, but retained the professorship, and until the close of his life in the quality of his work as an instructor he was unsurpassed, if not unequalled. Among our many distinguished teachers the foremost reputation, as we think, has by general consent been conceded to him. He had the great advantage of small classes, so that he could enter into familiar relations

with the students individually, and thus adapt himself to their respective modes and measures of receptivity. While he was President, his method was to take the Freshmen specially under his charge for the first term, and in the form of a recitation from some simple manual that required no elaborate study on their part or exposition on his, to talk to them and with them on a wide range of subjects bearing on their scholarship, character, and aims in life. His endeavor was to become thoroughly acquainted with them, and to bring them into intimate intercourse with himself. In subsequent portions of the college course, he frequently attended the recitations of the other teachers, and in case of their illness or absence was wont to serve as their substitute. Senior year he again took possession of the class, and in two or three separate courses he was their sole instructor. He trained them to think, and to express their opinions freely, on a wide range of subjects in mental philosophy, ethics, sociology, and civil polity. One of the results was that the essays on the stage at the Williams College Commencement showed a maturity and vigor of intellect that seemed hardly to belong to scholars still in their novitiate. Many strong and eminent men were trained under him, and there was not one of them who did not regard the educational services of President Hopkins as among the most important factors of his intellectual and moral character, and of his success in life.

Dr. Hopkins, after returning to Williams College, prepared himself for the Christian ministry, and received ordination. As a preacher he combined to a rare degree strength and beauty. His style is eminently forceful, yet rich in the unstudied graces of a mind attuned to all harmonies and endowed with the keenest æsthetic intuition. His services as a preacher were eagerly sought, and his published discourses have a permanent value, equally for the great themes that constitute their subjects and for the masterly treatment of those themes, whether in argument, illustration, or appeal to the individual conscience. He also published a series of Lowell Lectures on the Evidences of Christianity, and several series of Lectures on subjects belonging to the department of Ethics,—all of which are indicative of his profoundness of thought and of his didactic power.

Dr. Hopkins was for several years President of the American Board of Commissioners for Foreign Missions, and presided at the annual meeting next preceding his death, when he endeavored to act as mediator between the contending parties, though without the success that was justly due to his weight of character, his judicial fairness and impartiality, and the reverence which a presence like his could not fail to inspire.



Dr. Hopkins had a massive and rugged strength of body corresponding to his type of intellect. After he had passed his eightieth year he travelled extensively in Europe, and performed some of the most toilsome of the journeys in the mountainous regions of Switzerland. He attended the two hundred and fiftieth anniversary of Harvard College, and endured the fatigues of that season without a symptom of weariness. He continued his full class-work without intermission or faltering till the very day of his death.

In private life, in his home, and in society, Dr. Hopkins won no less affection than respect, for gentleness, kindness, hospitality, and the entire range of the peculiarly Christian virtues. No man can have been more, or more worthily, beloved, or would have been more lamented, had not his friends rejoiced that so noble an earthly life should pass on to heaven before the else inevitable infirmities of age had begun to enfeeble his body or to obscure his mind.

### CHARLES ELIOT WARE.

THE family of Dr. Ware has long been distinguished in this community. His father, Henry Ware (H. U. 1785), was for forty years Hollis Professor of Divinity, and his brother Henry Ware, Jr. was Professor of Pulpit Eloquence and Pastoral Care for thirteen years, in Harvard University. John Ware, another brother, for twenty-six years Hersey Professor of the Theory and Practice of Physic in the same University, was one of the most eminent physicians of Boston.

Dr. Ware was born on May 7, 1814, graduated at Harvard College in 1834, and three years later received the degree of Doctor of Medicine. He was well fitted for his calling by the clearness of his perceptions, by the soundness of his judgment, and by his industrious habits. He was well read in medical literature, and, while not departing from a wise conservatism, his mind was open to receive the new truths which are constantly presented by the rapid advance of medical science. He soon rose to the front rank of the profession, and acquired a large practice, which he retained for many years, until compelled by failing health to retire from active labor. He was for ten years one of the visiting physicians to the Massachusetts General Hospital, and on his resignation, in 1867, was appointed on the Consulting Staff. He was an influential member of the Board of Trustees, and Vice-President, of the Boston Lying-in Hospital. He took an active part in the various organizations for medical progress in Boston, and for six years was Secretary of the Massachusetts Medical Society. In conjunction with the

late Dr. Samuel Parkman, he established, in 1842, the New England Quarterly Journal of Medicine. In looking over the only volume of this periodical which appeared, one is astonished at its superiority, considering the state of medical science among us at that time. Many of the articles are of a high order, and could it have been sustained for a few years longer it would have done much for the progress of medicine in this country; but the mass of the profession were not able to appreciate its value, and it was discontinued at the end of a year from lack of support.

After his withdrawal from the practice of his profession, Dr. Ware spent many months of each year in the town of Rindge, N. H., upon a farm which he delighted to cultivate, where he died, on the 3d of September, 1887, aged seventy-three years.

# ASSOCIATE FELLOWS.

### SPENCER FULLERTON BAIRD.

PROFESSOR SPENCER FULLERTON BAIRD held at the time of his death three important scientific posts at Washington. He was Secretary of the Smithsonian Institution, Commissioner of Fish and Fisheries, and Director of the National Museum. He was born at Reading, Pennsylvania, February 2, 1823, graduated at Dickinson College in 1840, and was appointed to the chair of Natural History by his Alma Mater in 1845. In 1850 he accepted the position of Assistant Secretary of the Smithsonian, and removed to Washington.

Professor Baird was best known to science as a successful student of Vertebrata, and he is credited by Stejneger and Ridgeway with having originated the Bairdian school of ornithologists through his improvements upon the previously existing methods of research.

He had charge of the department of exploration in the Smithsonian, and was very influential in securing the connection of scientific workers with the numerous surveys sent out by the government, and took the most prominent part in the working up of the collections brought home by the earlier expeditions.

He also exercised a very large and beneficial influence upon the general progress of science in this country through his admirable management of the department of exchanges in the Smithsonian.



Professor Baird's private collection was the real beginning of the National Museum. His advent in the Smithsonian was immediately followed by the donation of this collection, and the initiation of a movement which, by slow degrees, finally led to the building and equipment of our National Museum, in 1882.

It was largely due to his work that the Bureau of Ethnology was established, and Major Powell placed at its head, in 1879, and the annual report of the Director is still made to the Secretary of the Smithsonian.

The Bureau of Fish and Fisheries was established wholly through his exertions and influence. Its services to science have been very marked, especially in the important work of exploration and description of the faunas of the coast. Its services to economical science cannot be fairly estimated at the present time, but even within the few years since it began experimenting, it has demonstrated that the boldness of its plan and the confidence of Baird in the resources of scientific investigation were well grounded. The Commission has shown that the prosperity of the fisheries and the supply of food fishes from our inland waters and rivers can be controlled, and, further, that we may also hope to be able to control the supply to be derived from the sea. Independently of their economic value, these facts are important additions to our scientific knowledge, and their influence upon the prospects of science through the respect thus cultivated in the minds of practical men has been very considerable.

Professor Baird's personal and social influence at Washington, and throughout the country, was in proportion to his great abilities and unselfish life.

The foundation of one institution leaves often an ineradicable impress upon the history of science. Professor Baird's record included the origin and early history of two institutions, and services of vital importance in the foundation of others. These are his monuments, and future generations will read in them the story of a life of devotion to research and the betterment of humanity, which will not fail to excite their admiration and gratitude.

# SAMUEL GILMAN BROWN.

REV. SAMUEL GILMAN BROWN, the son of Francis Brown, President of Dartmouth College, was born at North Yarmouth, Maine, January 4, 1813. He graduated at Dartmouth College in 1831, and at the Andover Theological Seminary in 1837. Though an ordained

Congregational minister he never had a pastoral charge. From 1835 to 1837, he was Principal of the Abbot Academy at Andover; from 1837 to 1863, Professor of Rhetoric and Oratory in Dartmouth College; from 1863 to 1867, Professor of Intellectual Philosophy and Political Economy in Dartmouth College; from 1867 to 1881, President of Hamilton College, at Clinton, New York. He resigned his presidency on account of declining health, and took up his residence at Utica, New York, where he died on the 4th of November, 1885. His principal literary work was "The Life of Rufus Choate." He delivered in Boston courses of Lowell Lectures on "The Earlier English Literature," and on "British Orators."

President Brown was a man of exquisite literary taste, master of a singularly chaste and pure English style, an able preacher, a thorough student, an accomplished scholar. As a teacher, he never failed to win the sincerest respect, gratitude, and affection of his pupils, and in Dartmouth College especially there is no memory of the present century more dearly cherished than his. He was a modest man, and was seldom seen except at his posts of duty and of public service; but to those who enjoyed his intimacy he seemed unsurpassed in the virtues and graces that command equal honor, reverence, and love.

## FOREIGN HONORARY MEMBERS.

# MATTHEW ARNOLD.

Among the eminent men of letters whose names have been borne on the roll of Foreign Honorary Members of the Academy during the past generation, not one has done more to affect the course of the deeper currents of thought in his time than Matthew Arnold. The writings of some others have, indeed, been more popular than his, and more widely read. But he has specially addressed the minds capable of receiving and of propagating the highest influences. No other English writer has attained such distinction in prose and in poetry alike, or displayed such equality of power as poet and as critic. Alike in poetry and in prose his aim has been "the moral interpretation, from an independent point of view, of man and of the world." In fidelity to this aim is the unity of his work as poet and as critic; for such interpretation is the great business of both.

He was the eldest son, and the second child of his parents, and was born on the 24th of December, 1822, at Laleham, near Staines, in Middlesex, where his father, then a man of twenty-seven years old, afterward to become so widely known and honored as the Head Master of Rugby School, was at the time residing. Dr. Arnold was appointed to Rugby in 1827, and removed thither with his family during the next For some years, while he was still a young boy, Matthew Arnold was sent to a private school at Laleham; but in August, 1836, he entered Winchester, where he remained for a year before being transferred to Rugby and brought immediately under his father's powerful influ-His poem of "Rugby Chapel," written in 1857, fifteen years after his father's death, commemorates justly those strong and high qualities of character, that fervent and heroic nature, which made Dr. Arnold not only a master of schoolboys, but a leader of men. In 1841 he went up to Oxford, having won the open scholarship at Balliol Col-At Oxford he was both popular and successful. The University was full of a fervent life, in which Arnold had a large share. In the opening of his Lecture on Emerson, written late in life, he has reproduced, in a passage of incomparable beauty, the impression of these Oxford days, and of the contemporary voices which appealed most strongly to his youth. In his first academic year he won the Hertford Scholarship, given for proficiency in Latin; he won the Newdigate prize for English poetry with a poem on Cromwell; but in his final examinations he was disappointed, and obtained only a second class. appointment was made up for, however, by his election in 1845, just thirty years after the election of his father, to a Fellowship in Oriel, at that time a College specially distinguished by the brilliant character of its Fellows. Newman, who in this very year left Oxford for Rome, was one of them. Among the others, to mention only those who have attained more than a University reputation, were Dr. Church, the present Dean of St. Paul's; James Fraser, the late admirable Bishop of Manchester; and Clough, who stood nearer to Arnold in friendship than any of the rest. Long afterwards Arnold commemorated this friendship and its associations with Oxford in his poem of "Thyrsis," - an elegy that ranks with the best that Greek or English poetry has to show.

Arnold was not disposed to enter the Church, and in 1847 he accepted the place of private secretary to Lord Lansdowne. This gave him access to the world of affairs, but his ruling taste for letters was manifested by the publication in the next year of his first volume, "The Strayed Reveller, and other Poems, by A." It had no great success, and

in the later collection and reprint of his Poems a large part of the contents of this volume is omitted. But a discerning critic might have recognized in it the qualities of a new, strong, individual genius. The hand had not yet attained full mastery over the instrument, but its touch was one of exceptional sensibility and refinement. The sentiment of the Poems was instinct with the modern spirit, but their form was largely shaped on the models of classic tradition. Arnold's poetry was the poetry of a scholar, but of a scholar in closest sympathy with the sentiment and emotions of his own generation.

In 1851, resigning his private secretaryship, he was married, and appointed to the post of Lay Inspector of Schools, a position which he held for most of his remaining life. It was a post of drudgery, scantily paid, of often wearisome routine, and of apparently narrow limits of usefulness. His professional work was little noted by the public, but he carried into it a spirit of such energy and wisdom that, subordinate as his position was, he became one of the most strenuous and powerful reformers of the system of school education in England, and one of the chief agents in bringing about the salutary and far-reaching changes which have been carried into practice during the last twenty years. In the series of Annual Reports published by the Committee of Council on Education a great part of the work of his life is to be found recorded. His contributions to these Reports have more than a transient interest: they belong to literature; they are, to use a phrase of his own, "saturated with thought."

In 1859, and again in 1865, he was sent to the Continent to study and report upon the system and condition of public education in France, Germany, and Holland; and in 1867 he published an important volume containing the result of his observations and investigations. But, notwithstanding the constancy of his official occupation, he found time for his chosen pursuits, and for the cultivation both of poetry and of learning. He published, in 1853, "Empedocles on Etna, and other Poems"; and in 1854, a volume made up partly of new poems, partly of a selection of those of his poems previously printed which he cared to pre-He was not a popular poet, but the impression made by his poetry upon select readers was deeper than that made by any contemporary verse. In 1857, he was chosen to the Professorship of Poetry at Oxford, and from this chair he delivered his Lectures "On Translating Homer," and "On the Study of Celtic Literature," which gave him the undisputed position of a master in criticism. The Preface to his tragedy of "Merope," in 1858, set forth ably his view of the true principles of criticism, which was illustrated by the volume, published a

few years later, in 1865, of his "Essays in Criticism." "A disinterested endeavor to learn and propagate the best that is known and thought in the world;" "in all branches of knowledge, theology, philosophy, history, art, science, to see the object as in itself it really is;" to know the best that is known and thought in the world, and, by in its turn making this known, to create a current of true and fresh ideas,"—this was Arnold's definition of the nature and business of criticism. It was a new and fruitful conception for the English mind. The first suggestion of it doubtless came to him from Goethe and Sainte-Beuve, but neither of them had formulated the method and motive of criticism with such precision. Subject, form, style, are not the final object of criticism, but the life they exhibit. It is the criticism of life that underlies all true criticism of books, of manners, of institutions. And it was as a critic in this sense that Arnold treated the deepest problems of our time, literary, theological, and social.

He held the Professorship of Poetry for two terms of five years, as long as under its statute it could be held consecutively by the same person. As years went on he wrote less poetry, and fewer essays on literary topics. He devoted himself mainly to the study and criticism of theological and religious questions. He was by nature deeply religious. The rapid growth of scepticism and unbelief among large sections of the English people, including many of the most thoughtful and serious minds, seemed to him largely due to the false notions prevalent in the churches, and embodied in their accepted creeds, as to the real nature of the Bible, and the true character of Jesus and of his teachings. He applied his critical method to the exposition of these subjects. He treated them with a free hand, but there could be no question of the seriousness and sincerity of his aim. His attempt, as he said, "was an attempt conservative, an attempt religious." His work has had great effect, and probably no single influence during the past twenty-five years has done more to lift the character of theological discussion from dogmatic advocacy of special doctrines to disinterested inquiry and investigation of the truth.

After a period of more than thirty years' service as Inspector of Schools, he retired from the place on a scanty pension, with the intent of giving himself more entirely to literature. In 1883–84 he visited America and delivered three or four striking and interesting lectures in many of our cities. But he was not fitted for a popular lecturer. His delivery did not do justice to his thought. His discourse, full of charm of style, full of literary distinction, and full of independent thought that required openness of mind for its just appreciation, fell coldly on audi-

tors accustomed to more mere rhetorical excellence. In private intercourse he made many warm friends, who were glad to welcome him again on a second visit to this country in 1886. In the interval between his two visits, and after his final return to England, he published several articles on America, embodying the results of his personal observations. They were as frank and independent as the criticisms of his own people had been from the beginning of his career. The same poetic sensibility of nature, the same breadth of cosmopolitan culture, which had made him susceptible to the clumsiness, the coarseness, the unintelligence, of the masses of the English people, - faults which he exposed and condemned with an essentially good-humored flow of wit, irony, and keen good-sense, - made him equally susceptible to the narrowness, materialism, and vulgarity of many of the aspects of American civilization. But his censorship was in both cases based on a large and truthful appreciation of the soul of excellence that exists beneath the unattractive shows and evil tendencies of the actual social order. wounds are sharp, but they are the salutary wounds of a friend. last words touching the matter, spoken two months before his death, are: "The English race overspreads the world, and at the same time the ideal of an excellence the most high and the most rare abides with it forever."

Still in the fresh enjoyment of life, still preserving the spirit of youth, death came suddenly to him on the 14th of April last. It was caused by inherited disease of the heart. The death of his father had been of like suddenness, from the same cause.

The great service of Arnold has been his steady assertion of the supremacy of the spiritual element in life, and his constant appeal to the higher intelligence. He has fulfilled the great function of the poet and of the critic,—the endeavor to interpret human life afresh in terms appropriate to the actual generation, and to supply it with the spiritual basis it requires.

To those who knew him intimately, Arnold was one of the most lovable of men. He was a delightful companion, — simple, cordial, cheerful, with great variety of interest in men and things. His tastes were those of an Englishman of letters, who finds culture as well as pleasure not only in books, but also in out-door things. His sympathies with dumb animals were deep. He had a tender and affectionate heart, and a pure soul. "The happiness at which we all aim," he said, "is dependent on righteousness." He had much happiness in life.

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#### GEORG CURTIUS.

GEORG CURTIUS, younger brother of the classical archæologist and historian, Ernst Curtius, was born at Lübeck in 1820. He studied classical philology at Bonn and Berlin, and in 1842 became teacher at the Blochmann Institute in Dresden. He early interested himself in the comparative philology of the Indo-European languages, at that time a new branch of inquiry, especially in its bearings on Greek, and his most important contributions to science were made in this field. His first book, issued in 1842, was entitled De Nominum Græcorum Formatione. Curtius's academic career began in 1846, when he became privat-docent in Berlin; in 1849 he was called to an extraordinary professorship at Prague, and in 1851 he was appointed Professor Ordinarius in the same institution. From 1854 to 1862 he was professor at Kiel; in 1862 he went to Leipzig to the professorship held through the first half of the century by the famous Gottfried Hermann (1809-48). This position he retained until his death, on August 12, 1885. Professor Curtius will ever hold an honorable place in the history of classical scholarship in Germany, in part through his own writings, and in part through the school of philologians founded by him. His principal works are his Grundzüge der griechischen Etymologie (1858-62, 1st ed.), and his Griechisches Verbum (1873-76, 1st ed.). He also wrote a Greek Grammar for schools (1852, 1st ed.), which, appearing in many editions, is now the most popular school Greek Grammar in Germany. Upon this work is freely based the Grammar of Professor James Hadley. In 1863 was published the Erläuterungen zur meiner griechischen Grammatik. Curtius's interests as a scholar were by no means confined to the study of the Greek language. He lectured, and wrote many articles and pamphlets, on subjects in classical literature, philology, and history, and on classical education. A collection of these essays has lately been made. As founder and as conductor of his Grammatische Gesellschaft at Leipzig through many years, Professor Curtius gathered about him a large number of men destined to become eminent as classical and comparative philologists; the first fruits of their work under his inspiration were in part collected in the Studien zur griechischen und lateinischen Grammatik (1868-77). Curtius was a pioneer in his work, and it is not surprising that some of his positions have been abandoned by the advancing scholarship of the younger generation. His writings, however, will long remain an indispensable part of the apparatus of the classical scholar. As a university lecturer Curtius enjoyed remarkable popularity; his style was simple, and his

method was the perfection of lucid and systematic demonstration. To Americans he always extended a most cordial welcome, and in the charming hospitality of his home he was ever seconded by his accomplished wife, familiarly known as Curtia. There are many of our younger scholars whose pleasantest and most stimulating associations with German scholarship are connected with the personality of Georg Curtius.

#### AUGUST WILHELM EICHLER.

AUGUST WILHELM EICHLER was born at Neukirchen, in Hesse-Cassel, on the 22d of April, 1839. After a gymnasial course at Hersfeld he entered the University of Marburg, where he devoted himself to the study of mathematics and the natural sciences, the latter under the guidance of Wigand. In 1861 he gained his doctorate, the subject of his thesis as candidate being "The Development of the Leaf, with especial Reference to the Formation of Stipules," which at once revealed his talent and promise. Upon Wigand's recommendation, he was now invited by Martius to Munich to be his assistant in the care of his herbarium, and soon became engaged with him upon his great work, the "Flora Brasiliensis," to which he contributed largely until the death of Martius, in 1869, when he himself assumed the editorship of it. From 1865 till 1871 he also gave private botanical instruction in the University of Marburg, and then accepted the position of Professor of Botany in the Polytechnic Institution at Grätz. In 1873 he was appointed Professor of Botany at Kiel, and five years later succeeded Alexander Braun as Director of the Royal Botanic Garden and Museum at Berlin, which office he held till his death, on the 2d of March, 1887.

Eichler's contributions to the "Flora Brasiliensis," which included the Gymnosperms, many of the smaller polypetalous orders, and several of the other dicotyledonous orders, were marked by extreme thoroughness, and established his reputation as an acute and skilful systematic botanist. These investigations led to the discussion by him of various morphological questions, especially in relation to the structure of the flower in the orders under review, and out of this grew the most important and prominent of his publications, the "Blüthendiagramme." In this strictly morphological treatise Eichler took up the phænogamous orders consecutively, and with much originality and painstaking accuracy gave in detail the peculiarities of many of the genera under each order in respect to the inflorescence, the parts of the flower, and their arrangement, illustrating the whole with numerous diagrams. The

work is unique in its class for its extent, completeness, and thoroughness.

Eichler was a man of strong will, having a great capacity for labor, and with a sensitiveness to duty which allowed him no rest so long as his physical strength endured. During the last ten years of his life, however, he suffered much from disease, which revealed itself in 1886 as the fatal malady known as leukæmia.

He was elected Member of this Academy in 1885, as successor to George Bentham. His name has been given to a Brazilian genus of Geraniaceæ.

## HENRY JAMES SUMNER MAINE.

SIR HENRY JAMES SUMNER MAINE was born in the year 1822. He was a son of the physician, Dr. James Maine. He was educated at Christ's Hospital, and at the University of Cambridge, where he received many honors for his excellent scholarship. The Craven Scholarship was given him, and medals for Latin and English verses. He was Senior Classic, Senior Chancellor's Classical Medalist, and Senior Optime in Mathematics. He took his degree in 1844. He did not receive a fellowship from his own College, Pembroke. There were no Pembroke fellowships vacant at the time. He received one from Trinity Hall, and took up his residence there. He was Tutor in the College, and afterwards, at a later period of his life, its Head Master.

Between the years 1844 and 1847 he must have been mainly occupied with the study of Jurisprudence; for in 1847 he was made Regius Professor of the Civil Law in his University. Three years later, in 1850, he was called to the bar, and became a member both of Lincoln's Inn and of the Middle Temple. At the Middle Temple he was Reader in Jurisprudence and the Civil Law, and delivered the lectures which were afterwards (in 1861) published under the title of Ancient Law. The lectures were delivered in the beautiful old hall of the Middle Temple,—the same hall where, in 1601-2, Shakespeare's Twelfth Night was performed.

The Ancient Law is almost the first book in our language in which Jurisprudence is treated from a strictly scientific point of view. It is almost the first attempt to explain the development of legal ideas according to the doctrine of evolution. The book is composed in a very simple and lucid style, so that it is interesting not merely to students of legal history, but to scholars generally; it has been very much read, both in England and in foreign countries; and it has brought

to its author a great and deserved reputation. In 1862, almost immediately after the publication of the Ancient Law, Maine was appointed legal member of the Government Council in India, and he accepted the appointment. This was the beginning of his connection with the government of India, — a connection which lasted until his death. Maine was in India seven years. He returned to England in 1869. Two years later he was created Knight Commander of the Order of the Star of India (K. C. S. I.), and at the same time was appointed a member of the Council of the Secretary of State for India.

Maine's academic work was laid aside during his absence in India, but he resumed it after his return to England. In 1870 he was made Corpus Professor of Jurisprudence at the University of Oxford,—the professorship being created especially for him. It was at Oxford that he composed some of his most interesting lectures. They were delivered in the hall of Corpus Christi College, to large audiences, made up mostly of graduates. Maine was a good lecturer, in spite of the fact that his lectures were always "chapters of books read aloud." The presence of the man was fine, his voice and manner were good, and we know how interesting the lectures were in matter, having read the books in which they were afterwards published; — Village Communities in the East and West (1871); Lectures on the Early History of Institutions (1875); and Dissertations on Early Law and Custom (1883).

In 1875 Maine gave the Rede Lecture at Cambridge on the Effect of the Study of India on Modern European Thought. In 1878 he delivered a lecture on Modern Theories of Succession to Property. He was a frequent contributor of articles to newspapers and magazines. Among the more important of the contributions to magazines are the Essays on Popular Government, which appeared first in the Quarterly Review, and afterwards (in 1885) in book form. Maine held his professorship at Oxford until 1878, when, being appointed Head Master of Trinity Hall at Cambridge, he returned to his own University. Last year he received at Cambridge the Whewell Professorship of International Law, and gave one course of lectures on this subject. His usefulness in Cambridge was not, however, limited to his lecturing and teaching there. His personal influence over his College, and over the whole University, was good in every way, and his loss will be deeply and sadly felt.

In 1849, just before he was called to the bar, Maine married his cousin, a daughter of George Maine. They had three children, two of whom, both sons, are living.

Maine was never a strong man. As a youth he was frequently ill. His stay in India benefited him in respect to his health, and he was stronger after his return. He was well enough, as a rule, to work moderately hard, and to perform satisfactorily the duties of his various appointments. But early in this year, 1888, he felt very feeble and nervous, and decided to go to the South of France for a rest. On the 3d day of February, while he was at Cannes, he had a stroke of apoplexy, and died in a few hours. He was buried at Cannes on the 8th.

Sir Henry Maine was a Fellow of the Royal Society, a Foreign Associate of the Institute of France, being chosen in the place of Emerson, and he was elected Foreign Honorary Member of this Academy, November 14, 1866, in place of Whewell.

Having reviewed the principal events of Maine's life, we must now consider his life's work, its character and its value. The work distributes itself into two departments, one of scholarship, and one of statesmanship. Maine spent as much as half of his life's energy in connection with the government of India. As legal member of the Government Council, an office previously held by Macaulay and subsequestly by Fitz James Stephen, Maine drafted many important statutes. Among others, the Successions Act and the Marriage Act of 1865; the Companies Act of 1866; the General Clauses Act of 1868; and the Divorce Act of 1869. These statutes, particularly the Successions Act, are described as models of comprehensive thought and direct expression. No one, however, not an expert in Indian affairs can speak with authority regarding them. Nor is it possible for us to estimate the value of Maine's work as adviser of the government in its councils, commissions, and committees. We can only record what we have heard from others who were associated with him. They speak of him as a man of great good sense and wisdom, a man who kept his temper under all circumstances, and a most pleasant man to be associated with.

We hear of certain complaints of office clerks, who say that Maine was very unwilling to do routine work and shirked it when he could. It is well that he did so. A man of Maine's mental power and capacity of understanding ought not to waste his energies in routine work, which is mostly thoughtless work, when there are so many people everywhere who are especially fitted for it. We must remember that Maine was not a strong man, physically; he had to save his strength as much as possible. Perhaps he was not a hard worker, in the ordinary sense of the phrase; but he was certainly a hard thinker.

Maine was naturally a very quiet man; he disliked publicity; he liked to do his work, whatever it was, in a private way. He avoided public life and public speaking. When at one time it was proposed that he should go into Parliament, as representative of Cambridge, he declined; and when Mr. Gladstone offered him the office of Chief Clerk of the House of Commons, after the resignation of Sir Erskine May, he declined again. He was willing to serve the public, and did so in connection with the government of India, and in all the work of his life, indeed; but his service was done very quietly and unostentatiously. Maine was in temper cautious, not to say timid, and very conservative. He was always ready and willing to discuss a state of affairs, and he was willing to suggest measures of reform and change; but he did not like to commit himself even to the measures he suggested, and objected to taking any leadership in connection with them. Maine liked to hold his judgment free: he would state an opinion and state it distinctly; then he would qualify it with an if or a perhaps. This characteristic is plainly exhibited in all his writings. It is very irritating to those who like to engage in personal controversies. They take up Maine's opinions, and argue against them, as his opinions. Then he says that they were rather suggestions than opinions; and that he never invited, nor proposed to enter into, any controversies regarding them. Maine disliked personal controversies, and avoided them as much as possible. We have seen a letter he wrote some years ago, in which he objects to the method of a certain teacher of history, who was in the habit of encouraging his pupils to enter into controversies. Maine objected to anything like enthusiasm or zeal in the pursuit of scientific truths. He himself worked in a very quiet, cautious, conservative spirit, and wished to have others work in the same spirit. He held to the principle, that it is not men we have to quarrel with in this world, but false and injurious ideas, which the very best of men may hold with the best of motives. We gather another principle out of Maine's life, - that we are responsible, not for other people's ideas, but for our own. It is our own ideas which we must look after and correct and perfect, not those of other people. Maine was not a man to undertake or to carry out reforms. The successful reformer must be sure of his views, confident of his cause, and he must be eager to defend his cause against every form of opposition, and zealous in getting other men to take it up and help defend it. Maine longed not so much to establish his views as to correct them. He was always expecting out of one idea to get another and better one. So he kept his mind, not in the state of conclusion, but in a state of

transition from one idea to another. Maine's disposition and temper of mind were essentially scientific and scholarly. Maine's work as a statesman was the work of a scholar and literary artist in the field of statesmanship. He drafted statutes, he formulated opinions on political questions, and expressed them finely, but his motive was, in all this work, scientific and artistic, not practical.

It is as a scientific man and as a man of letters that Maine will be remembered, not as a statesman. He will not be remembered as the man who drafted certain statutes and gave his advice in connection with the government of India, but as the author of the "Ancient Law." The Ancient Law is certainly one of the great books of this century, remarkable in its contents and in its consequences. The book was published in 1861, only fifteen months after the publication of Darwin's Origin of Species. There is an interesting and significant connection between the two books. We have in Darwin's work the application of the doctrine of evolution to the history of organic life. Maine's work the application of the same doctrine to our intellectual life in some of its chief phases or aspects. A new purpose and a new method of study were given to students in the field of custom, law, and politics. The purpose was to explain existing social, legal, and political ideas according to a theory of evolution, development, diversification, or differentiation. The new method of study by which it was proposed to discover the natural order and succession or generation of social, legal, and political ideas was that which Darwin had employed to discover the order in which organic forms in plant and animal life have been evolved. It was the comparative method of the naturalist. The method is described by Maine as follows. "We take," he says, "a number of contemporary facts, ideas, and customs, and we infer the past form of those facts, ideas, and customs, not only from historical records of that past form, but from examples of it which have not yet died out of the world and are still to be found in it. . . . Direct observation comes thus to the aid of historical inquiry, and historical inquiry to the help of direct observation."

Of course the question comes up whether this method is applicable to the phenomena of mind, whether we can hope to explain by it the developments of the human intelligence, and find out what were the primitive, elementary thoughts and practices of mankind. Our ideas are very largely the result of external conditions and circumstances. They are composed out of experiences, and experiences differ. It might be inferred from this that the comparative method would be inapplicable to the field of intellectual life. We might not expect to dis-

cover any regular order in the development of ideas. We must not forget, however, that among the external conditions and circumstances according to which our ideas are formed are to be enumerated all the traditions, practices, and works of our forefathers, which in one way or another express their ideas. So it happens that the thoughts of one generation of men are very largely determined by those of preceding generations; and we discover in the study of historical records that there has been in every branch of the human race a very regular order in the development and diversification of ideas, corresponding remarkably well with the development and diversification of physical characteristics among plants and animals. When, therefore, we know from similarity of physical characteristics that two races were once associated in a common origin, we infer by a very sure hypothesis that they started in their independent existence with certain common ideas and common practices, and the question arises, What were these ideas and practices? The comparative method is the method which we employ in trying to answer the question. We must, however, in order to reach any certain results by means of the comparative method, have clear, unquestionable, early records, on the one hand, and well understood ideas and practices on the other, and an unmistakable coincidence between them. Early records are apt to be few and doubtful in character, and it is very difficult, often impossible, for a civilized man to understand the ideas and practices of savages and barbarians; so it is very improbable that we shall reach any trustworthy conclusions in regard to the beginnings of intellectual life and the origin of human society. This was clearly Maine's idea. He says: "It was no part of my object to determine the absolute origin of human society. I have written few pages which have any bearing on the subject, and I must confess a certain distaste for inquiries which, when I attempt to push them far, have always landed me in mud-banks and fog." We may not be able, perhaps, to solve the problems of primitive life by the comparative method, but there are innumerable very interesting developments of the human intelligence which we can make out clearly. Maine has described some of these developments in a most striking and interesting way, in his Ancient Law, and in the books which were published during the period of his Oxford Professorship, - Village Communities, The Early History of Institutions, and Early Law and Custom.

Some of Maine's theories have met with adverse criticism. His theory that the patriarchal idea is a primitive idea has been opposed by a number of well known and able writers, who maintain that the primitive social unit was not the family under the headship of the father, but the horde, - "a company of men and women in which the relations of the sexes were wholly unregulated at first, but passed through various stages of limitation or restriction until the family, patriarchal or other, was reached." Maine did not, I think, maintain that the patriarchal idea was the only idea governing the organization of primitive society. but he maintained that it was one of the governing ideas, and one of the most important. It was not an idea reached, but an idea started with. His arguments upon this theme are to be found in his Early Law and Custom. Another theory which has met with adverse criticism is the theory that the Russian mir, with its periodic redistributions of land in equal lots, gives us an idea of the primitive village community. Maine's theory is that private property in land has arisen in consequence of the "disentanglement of individual from collective rights"; that the earliest form of landed property is found in a kind of communistic partnership. The theory which is opposed to this one is, that the idea of personal and private ownership is at least as ancient as the idea of collective ownership. It is suggested that a communistic partnership among kinsmen means simply that an inheritance, once the holding of an individual, is not yet divided. As for the Russian mir, it leads us neither to one theory nor to the other. Since Maine first wrote about it, it has been shown to be in its present form a comparatively modern institution. The redistributions of the land into equal lots appear to be the result of a system of equal (per capita) taxation. The practice cannot be traced back more than two or three hundred years. village community of India, in which the land is a partly divided, partly undivided inheritance, may be regarded as the earlier type of village. Another of Maine's theories which may be objected to is the theory that "the typical manor arose out of the village community." It has been maintained, against this view, that the two institutions, the manor and the village community, arose side by side, and then one or the other became dominant. It is as easy for the manor to become a village community as for the village community to become a manor. When the manorial estate is divisible among the heirs, it tends to become a village community. When the chieftainship over a village community becomes hereditary, but is indivisible, the village community tends to become a manor.

In view of all these theories and counter theories, and of the fact that a great deal can be said in support of every one of them, on both sides, we cannot but feel that the object of historical researches is not so much to find out the order in which ideas have occurred to mankind, and the chronological sequence of human institutions, as it is to find out, first, the consequences of certain ideas, what institutions they give rise to, and, secondly, the consequences of certain institutions, what ideas they suggest.

The works and institutions of a people are expressive of its ideas. They are the monuments and records of its intellectual life. At the same time, the ideas of a people are determined almost wholly by its works completed and institutions established. Ideas produce institutions, and institutions produce ideas. So the question for the historian and philosopher is what ideas have produced the best institutions, and what institutions have produced the best ideas; for we want to cultivate the ideas which have had the best issues, and we want to establish the institutions which give us the best ideas.

Perhaps Maine had some such thoughts as these in his mind when he wrote his Essays on Popular Government. He takes up in these essays the idea of popular government, the idea of democracy, and he describes its growth and the institutions to which it has given rise. When the book was published, first in the Quarterly Review and afterwards in book form, it was described as "a rattling Tory pamphlet under the disguise of philosophy." Mr. John Morley is, I believe, responsible for the epigram. It is amusing, but inapplicable. The book is a compendium of Maine's political philosophy, written, as all his books were, without any practical motive or purpose, and with perfect sincerity. Maine takes an unfavorable view of popular government. He surveys its history, and observes that it is not an energetic form of government, not efficient, not economical, not very successful. He concludes that a democratic assembly is incapable of governing a great nation as it should be governed. He says that the most successful form of government has been, not that of the many, but that of the few. This is all very true. Democracy considered simply as a means of government is not very active, efficient, or economical. It is spendthrift both of mental and of physical forces. Nor has it been in the experience of the past very successful as a means of government. we must not consider democracy as a means of government simply. is much more than that. It must be regarded as an educational institution. Here lies its highest utility and surest success. Democracy is the most comprehensive educational institution that has ever been established.

Taking Maine's point of view, and considering democracy merely as a means of governing states and nations, we may, reasonably enough, agree with him. But we need not take his point of view. Instead of considering merely the institutions to which the idea of democracy has

given rise, we may consider the ideas which have arisen in consequence of the establishment of democratic institutions. What has been the effect of these institutions upon the human mind? Have they not had a great and noble effect? Can the institutions of monarchy and oligarchy show anything like it? Maine's view of popular government seems to us a narrow and very unsatisfactory one. It is in the field of historical inquiry and theory that we follow Maine with most profit. It is in this field that he did his best work, - discovering and describing historical developments, and making them interesting to pupils and We see in Maine almost the ideal teacher. There are two kinds of teachers, - those who give us knowledge, and those who give us the love of knowledge. These last are the best teachers, and Maine He was not merely an investigator, a collector of is one of them. facts and statistics. He was also an artist. He was able to compose the facts and statistics which he gathered together into interesting Here lies the secret of his great reputation and success. Other men have studied the records and survivals of the past as diligently as he; some men have surpassed him as investigators. He was sometimes a little careless in accepting statistics without verifying them, without tracing them to their original sources, and making sure of them. He was not so patiently laborious in the examination and criticism of historical records as some of his contemporaries; but he surpassed them all in the art of composing his materials into interesting and significant ideas. He was a man of imagination, - of comprehensive imagination. More than that, he was discriminating in regard to the materials out of which he composed his ideas. Nothing is easier than the composition of ideas out of facts, when one has imagination. Wherever there is imagination, there is a plentiful supply of ideas; but it does not follow that the ideas are in any high degree significant or valuable. value of an idea depends upon the importance of the facts or statistics which it comprehends. No one has ever understood this better than Maine. "All generalization," he says, "is the product of abstraction; all abstraction consists in dropping out of sight a certain number of particular facts, and constructing a formula which will embrace the remainder; and the comparative value of general propositions turns entirely on the relative importance of the particular facts selected, and of the particular facts rejected. The modern facility of generalization," he adds, "is obtained by a curious precipitation and carelessness in this selection and rejection, which, when properly carried out, is the only difficult part of the entire process. General formulas which can be seen on examination to have been arrived at by attending only to particulars, few, trivial, or irrelevant, are turned out in as much profusion as if they dropped from an intellectual machine." Maine shows not only a great power of imagination, but very unusual discrimination in regard to the materials he allows his imagination to work upon. The result is, that his ideas, and the writings in which they are so well expressed, have a permanent interest and value.

### HUGH ANDREW JOHNSTONE MUNRO.

An inadvertence has caused the retention on our honorary roll of the above name, although in point of fact its bearer died at Rome on the 80th of March, 1885. At the time of his decease he ranked as the first Latin scholar in the British Empire, and was recognized as the compeer of the best classical scholars in the world.

Hugh Andrew Johnstone Munro was born at Elgin, Scotland, in 1819. His education as a boy was mainly conducted at Shrewsbury School, under Dr. Benjamin Hall Kennedy as Head Master. Shrewsbury School is not so famous as Winchester and Eton, as Westminster or Harrow; and certainly it has to Americans none of the somewhat factitious renown which they have learned to attach to Rugby. But at the English Universities, and among cultivated Englishmen generally, Shrewsbury has a fame second to no school for producing first-rate scholars; and it would be hard to convince any pupil of Dr. Kennedy's that he had ever had his superior among the schoolmasters of England.

The taste and practice of the Shrewsbury scholars ran always in the direction of rigid accuracy rather than varied reading. Munro preserved the school traditions as to the first; but he bettered the instruction as to the second. Few scholars have been broader.

He entered Trinity College, Cambridge, in 1838; was chosen Craven University Scholar in 1841; was "Senior Optime" (second class) in the Mathematical Tripos of 1842, and Second Classic and First Chancellor's Medallist in the same year. His successful competitor for the highest classical honors was the Hon. George Denman, now Mr. Justice Denman, a son of Queen Caroline's defender, Lord Chief Justice Denman. Munro became a Fellow in 1843; and as he never married, and took orders in the Church of England, he retained his fellowship till his death.

Munro was in due time chosen on the staff of instruction in his college, and gave early proof of his powers as a critic by a paper before the Cambridge Philosophical Society, in which he contested Dr.

Whewell's views on some passages of Aristotle. The Master of Trinity occupied at that time a very distinguished position, and it was not well for any one to encounter him who was not sure of his ground. But Munro had pre-eminently the Cambridge characteristic, that he would not publish except when he did feel sure of his ground; and, on this first appearance, even those who disputed his conclusions could not question his perfect familiarity with his matter.

In 1854 was started the "Cambridge Journal of Classical and Sacred Philology," which ran through four volumes, the last appearing near the beginning of 1860. Munro was from the first a most important contributor to its pages; and when, after an intermission of nine years, it was resumed under the name of the "Journal of Philology," he renewed his articles, and continued to write for it at intervals until his death.

These articles took a sufficiently varied range in classical criticism, both textual, philosophical, and literary; and they exhibit throughout one of Munro's marked traits, that he was a student of literature in general. He was as familiar with Spenser, with Dante, and with Goethe, and as thoroughly provided with all the linguistic, historical, and æsthetic tools needed for their comprehension, as with Euripides and Catullus; and while his studies fell into the line of poetry rather than prose, no one who ever discussed a philosophical problem with him could doubt that the toughest reasoning was as handy to him as the tenderest melody. Shrewsbury, like the other great English schools, holds closely to the tradition that the practice of writing Greek and Latin verse is the best method for teaching accurately the form and body of those languages; and the volume of such compositions by her alumni, entitled Sabrinæ Corolla, contains many admirable pieces by Munro.

Among his earliest contributions to the above-named periodicals was an article "On some Passages in Lucretius." The recent editions of Lachmann and Bernays had directed the attention of scholars all over the world to this most remarkable writer, of whom English scholars could not exactly be said to be ignorant; but they knew him chiefly from the uncouth volumes of Wakefield. An entire revolution in the criticism of the text had been hinted at by Madvig, and fairly created by Lachmann; and many were disposed—as some are disposed even now—to accept the edition of the latter as a practical finality. Munro, in his first and subsequent articles, paid all possible honor to the learning, the diligence, and the intelligence of the great Prussian; but he showed plainly that his recension of the text was far from a final one; that in the interpretation of the poet Lachmann had done comparatively little, and that little very seriously in need of

revision; — in plain English, that a new edition of Lucretius was imperatively needed for the matter, if not for the text. In 1860 he issued the latter in a very handy form, introducing not a few important corrections; and in 1864 appeared his first real edition, — a revised text, an elaborate commentary, and an English prose version. A second edition, in a somewhat different form, and with many important corrections and additions, appeared in 1866; a third, revised with still more devoted care, was issued in 1873; and a fourth, with some slight additions to the commentary, has appeared since his death, in 1886, under the care of Mr. J. D. Duff.

In 1867 Munro issued from a manuscript in the Cambridge University Library an edition of the strange philosophical poem entitled Ætna. In 1868 he published, in connection with his colleague, the Rev. C. W. King, a very admirable text of Horace, issued in magnificent form, and strikingly illustrated, through the care of his collaborator, with engravings from ancient gems, in which Mr. King was an unrivalled expert. In 1871, Munro brought out a valuable tract on the newly-proposed Latin pronunciation; and in 1878, he collected a number of his papers in the Journal of Philology into a volume of "Criticisms and Elucidations of Catullus," containing some of his most striking views. In 1869 he was appointed to the newly constituted chair of Latin, which had been founded as a memorial of his master, Kennedy. But university lecturing was not to his taste, and he resigned the professorship in two years.

Munro's death occurred, as has been said, in Rome; he had gone in search of health to Italy in the spring of 1885, which proved unhappily inclement. Italy was known ground to him; he had collated the great manuscripts of Lucretius at Florence and Rome in 1851, and now in his closing days he enjoyed exploring the excavations of antiquities in the imperial city; but the murderous fever, of which no one who has not felt it knows the horrors, carried him off on the 30th of March. He lies buried near Keats and Shelley, in the famous Protestant cemetery close to the Pyramid of Cestius.

Munro was a man of short, stout frame, with a true North Country expression, and a manner curiously compounded of shyness and vivacity. His intimate friends were few, but most devotedly attached to him. His habits and character were those of the scholastic hermit, and it took a little courage to penetrate into his book-lined cell, which was that of a truly fastidious scholar. He did not talk till quite sure of his company. But to those who might and did press within the veil, nothing could surpass the impression made by the immense extent of

his learning, the firm grasp which he held on it, and the peculiar subtlety of his penetration, reminding one of Goldsmith's description of Burke, "winding into the heart of a subject like a serpent." He would have been terrible to encounter as an antagonist, were it not for a singularly courteous suavity which disarmed all resentment. There are passages in his works which, as we read them, savor of a pretty positive dogmatism; but one who knew the author can well conceive that from his lips they would have sounded even gentle. To a still more intimate circle, his counsel, his heart, and, if necessary, his purse, were open; and, as he never hesitated to lay before the learned world whatever he felt could be understood in its real meaning, so we are assured by those who knew him best that nothing in his great nature was not freely given where it would be valued.

He was unquestionably a very great scholar. He was a master in his honored art, — the art of criticising and expounding the treasures of the two great languages of the Mediterranean nations; the greatest Latin scholar of the century in England, and second to none of her classical giants since Porson; like him, a worthy descendant of Bentley, the great Master of what even the dry pages of the "Cambridge Calendar" cannot help calling a "noble and magnificent college."

Munro's fame will rest on his Lucretius, a monumental work; unlike many monuments, not a mere tombstone, but the perpetuator of a life as lively as that which breathes from Michael Angelo's statue of Lorenzo. Lucretius is a very great author, well deserving an editor of consummate ability. Scholars of the very highest erudition and taste, Marullus, Lambinus, Isaac Vossius, Gassendi, Bentley, Madvig, and Lachmann, have all stamped on his criticism and interpretation the impress of their peculiar genius. It is unfortunate that, in the intervals of their labors, many less worthy handled him; - Pius and Gifanius, Nardi and Havercamp, Wakefield and Forbiger, besides such moderate contributors to his elucidation as Le Febvre and Creech. To all this line of editors — a line beginning, says tradition, with no less a person than Cicero himself - Munro contributed a comprehensive erudition, a brilliant acuteness, an unwearied patience, which the greatest of them might envy. He added also a candor which recognized worth everywhere, and would submit over and over again his most cherished views to every test in order to arrive at the real truth, sacrificing them, if need be, without a murmur. A peculiar fastidious delicacy, the direct result of that practice in classical verse composition which German and American scholarship rejects to its irreparable loss, gave him a discriminating tact as to text and interpretation which Lachmann at the summit of his powers never knew. He possessed one quality coming directly to him from the matchless Bentley, the power of making his notes interesting. His Lucretius is a book that one enjoys reading. His conspectus of the manuscripts and editions, though avowedly a recasting of Lachmann's preface, is as charming an improvement over the Prussian's austere Latin as Livy's versions over Polybius. If one wished to lead the ordinary Latin student, filled with a schoolboy's knowledge of Virgil, Cæsar, and Cicero, and a sophomore's taste of Horace, Livy, Tacitus, and Terence, into a real love and thirst for true scholarship, the wisest course would be to set him down to Munro's two prefaces.

It must be allowed that Munro's intense study and acuteness sometimes deceived him; he would occasionally work so long and thoughtfully over a passage, that, like Dante, he got past the point of attraction, and, on the other side of the centre, saw the object with feet reversed, actually declaring a view unmistakable which to other men was simply an ingenious impossibility.

To the full he appreciated, he comprehended, he absorbed, his author. The antique purity of the diction of Lucretius, the stern melody of his verse, the vivid fertility of his imagination, the keen sweep of his observation, the close texture of his reasoning, the passionate force of his convictions, the undaunted loftiness of his aim, appealed to Munro, as they had to the greatest scholars before him,—to Scaliger and to Goethe,—with irresistible power. Even those of us who cannot surrender our love for the richer harmony, the more individual humanity, the more confiding faith, the more historical imagery of Virgil, will feel our admiration for that poet who was Virgil's immediate master, scarcely less than was Homer, deepened, strengthened, and widened by the work of his last—and why not his best?—editor.

This notice may seem too long; but it could not be shortened. That line of study which Munro made his own has to struggle in this country against the claims of what are considered more truly the arts of progress. When, then, a man, whose mind was fully capable of winning brilliant triumphs as an explorer in the realms of science or philosophy or history, devotes himself to criticism and interpretation so perfectly that all his work sparkles with the lustre of genius, it becomes the votaries of every science to admit in their journals an unstinted tribute to their brother.

"Carmina quin etiam divini pectoris ejus Vociferantur et exponunt præclara reperta Ut vix humana videatur stirpe creatus."

YOL XXIII. (N. S. XV.)

#### GUSTAV ROBERT KIRCHHOFF.

GEHEIMBATH GUSTAV ROBERT KIRCHHOFF was elected a Foreign Honorary Member of this Academy on November 9, 1870, to fill the vacancy created by the death of the eminent chemist. Thomas Graham. Kirchhoff was born in Königsberg, Prussia, on March 12, 1824. He died in Berlin on October 17, 1887, at the age of sixty-three years. After passing through the Gymnasium he continued his studies, in physics under F. E. Neumann, and in mathematics under F. J. Richelot, both eminent Professors in the University of Königsberg, taking his degree in 1847. At the age of eighteen he had selected the study of physics as his life work. As Privat-docent he started on his career of teaching and investigation, in Berlin. He was Professor Extraordinary and co-director of the Physical Institute in Breslau from 1850 to 1854. Here he formed a lifelong intimacy with the distinguished chemist, R. W. Bunsen. In 1852 Bunsen went to the University of Heidelberg as Professor of Chemistry, and Kirchhoff followed him in 1854, succeeding P. G. Jolly, who had gone to Munich, as Professor of Physics. Here he remained until 1875, when he was appointed Professor of Mathematical Physics in the University of Berlin.

This interesting description of Kirchhoff at the age of thirty, as given by Robert von Helmholtz, is quoted from the Popular Science Monthly:—

"There was, therefore, some surprise in Heidelberg when the slender, remarkably youthful, modest, even bashful North German appeared, heralded by Bunsen's warm recommendations. His refined, animated speech, his courteous and attractive demeanor, his fine sense of humor and his wit, soon won him the liking of all men with whom he came in contact. He was, therefore, a welcome participant in all the social gatherings of the circle into which he fell. His friendship with Bunsen became very close. Bunsen was thirteen years his elder, strong and broad-shouldered, with a lively, commanding temperament, making his influence felt upon every one. The two men were thus quite different in their outer aspects from one another: yet they not only pursued their great works in common, but also lived their daily social life together. They took walks in company in the environs of Heidelberg, and they travelled together during the vacations."

Before taking his degree, Kirchhoff had begun his work in original research, and published a remarkable paper on electrical conduction in a thin plate, especially a circular one. His problem was to find the current in any branch of a network of linear conductors. Starting

from Ohm's familiar law, he derived two results long recognized in electrical science as Kirchhoff's laws. Between the years 1845 and 1852, thirteen other papers appeared, discussing mathematically the most difficult problems in electricity, magnetism, light, heat, sound, and elasticity in general. In 1882, when the number of his separate publications had grown to thirty-eight, Kirchhoff gathered them together, from the various periodicals in which they originally appeared, into a volume of six hundred and forty-one pages, classifying them according to subjects, and chronologically in reference to each subject. The title of this volume is Gesammelte Abhandlungen, Leipzig, 1882. Out of a wide range of physical problems, all of which are treated with great mathematical skill, only a few salient points can be indicated in this notice.

Ohm deduced his laws for electrical currents from assumptions which are not in agreement with those required by the facts of statical electricity. Kirchhoff proves that Ohm's laws can be derived from the electrostatic repulsion of electricity by bringing to his aid certain assumptions in reference to the question which in the electrostatic theory remain open. Neumann and Weber trusted to experiment for the value of the constant on which the intensity of induced currents depends. In 1849 Kirchhoff obtained this constant by a purely analytical treatment of the subject, and thereby made the measurements of electrical resistance absolute.

In 1877 Kirchhoff published his theory of the motion of electricity in subterrene and submarine telegraph wires. He begins with the statement that Sir William Thomson had already, in 1855, starting from the hypothesis that the influence of induction, consequent on changes in the intensity of the current, could be neglected in comparison with the influence of the changes, reached the position that the electricity in such wires was propagated according to the same laws as conducted heat. He says: "I allow myself to lay before the [Berlin] Academy a derivation of this law, which rests upon the same hypothesis, but comes out from more general principles than those given by Thomson, and to annex some formulas which, so far as I know, have not yet been published."

In 1859 Kirchhoff began his work in optics by measuring the angle between the axes of aragonite for rays corresponding to the different Frauenhofer lines. Then, with Bunsen, he studied the spectra of colored flames, and recorded the rays, present or absent. Facts then appeared, he says, which gave an unexpected solution to the origin of the Frauenhofer lines, and justified inferences as to the material quality

of the atmosphere of the sun, and perhaps also of the stars. "I conclude from these observations that colored flames, showing sharp, bright lines in their spectra, so weaken rays of the same color which are sent through them that dark lines take the place of the bright ones, if a sufficiently strong light, deficient in these bright lines, is placed behind the flame. Furthermore, I conclude that the dark lines of the solar spectrum, which are not produced by the earth's atmosphere, are evoked by the presence of such substances as would in the spectrum of a flame exhibit bright lines in the same places."

Again he says: "I take this opportunity of stating a conclusion which I have reached since my earlier communication. According to the investigations of Wheatstone, Masson, Angström, and others, we know that in the spectrum of the electric spark bright lines appear, depending on the nature of the metals between which the spark occurs, and we may suppose that these lines coincide with those which would exist in the spectrum of a flame of very high temperature if we brought into it the same metal in a suitable form. I have examined the green portion of the spectrum of the electric spark between electrodes of iron, and have found in it a great number of bright lines, which seem to coincide with dark lines of the solar spectrum. In single lines the coincidence is hardly established securely, but I think that I have seen it in many groups, the brighter lines in the spark-spectrum corresponding to the darker lines in the sun's spectrum: I venture to conclude that these coincidences are not merely apparent. If the spark is taken from other metals, for example, from copper electrodes, these bright lines are wanting. I feel justified in concluding that among the ingredients of the glowing atmosphere of the sun iron is found: a conclusion which otherwise comes very close when the frequent occurrence of iron in the earth and in meteoric stones is considered."

This paper was followed, two months later, by another on the relation between the emission and absorption of light and heat. From the mechanical theory of heat Kirchhoff demonstrated mathematically the law that the proportion between the powers of emission and absorption is the same in all bodies at the same temperature, and for waves of the same length.

In 1860 Kirchhoff and Bunsen published a long paper under the title of "Chemical Analysis of Substances by Observations on their Spectra." This paper was illustrated by two plates; one representing the arrangement of the apparatus employed, and the other showing the spectra of six substances in juxtaposition with the solar spectrum. Of this work Kirchhoff writes: "From this comprehensive and prolonged investiga-

tion, the details of which I may be permitted to pass over, it comes out that the different combinations in which the metals have been tried, the variety of chemical processes in the different flames, and their vast difference of temperatures, exert no influence on the position of the lines in the spectrum of the same metal."

The last subject introduced into the Gesammelte Abhandlungen is the history of spectrum analysis and the analysis of the sun's atmosphere. It rarely happens to any great epoch in science that it comes wholly unheralded. Kirchhoff has candidly reviewed the various claims which have been advanced as anticipations of his discovery. Some of them were merely conjectures; others failed from too great generality and looseness of statement; the best circulated from mouth to mouth, were not published, and could not have been known to Kirchhoff previous to his own discovery; and all relied on inadequate experiments, unsupported by mathematical demonstration. great discovery in science, after it has been clearly proved and publicly announced, throws back a light upon its antecedents which they did not and could not originate. Spectrum analysis, with its far reaching consequences, was in the air: a few great minds felt it and predicted it; Kirchhoff demonstrated it.

In 1874, Kirchhoff published the Vorlesungen über Mathematische Physik, or "Lectures on Dynamics." These lectures, thirty in number, relate to the mechanics of solids and liquids, the theory of light, electricity and magnetism, and special subjects in hydro-dynamics and electro-dynamics. As Kirchhoff informs his readers in the Preface, he discusses what the phenomena are, and not their causes. Other writers are accustomed to define mechanics as the science of forces, and force as the cause which produces or strives to produce motion. Kirchhoff admits the usefulness of this definition in the development of mechanics, and to the student when it is illustrated by the experiences of ordinary life; but he thinks that there always clings to it an obscurity from which the idea of cause and resistance cannot be extricated. This obscurity manifests itself in the different views taken of the laws of inertia and the parallelogram of forces, whether they are the results of experience, axioms, or laws which can and must be known logically. Kirchhoff aimed to remove this obscurity from mechanics, even if it were only possible by a limitation of its propositions. He would describe, fully and in the simplest manner, the motions occurring in nature, ignoring their cause. Starting with the conception of space, time, and matter, he would arrive by purely mathematical paths at the general equations of mechanics. The notion of force comes in, but it is

not necessary to give a complete definition of it. But the imperfection of this definition introduces no obscurity into results; for the introduction of forces in this way only serves to simplify the modes of statement, and to express briefly equations which without the help of this name would be clumsily described by words. It is sufficient for removing all obscurity, to give so wide a definition to forces that every law of mechanics in which forces are named can be expressed by equations: and this happens in a striking manner.

Of Kirchhoff and his lectures Robert von Helmholtz writes thus, as translated in the Popular Science Monthly: "His favorite work, and the one having the most enduring results, was his lectures on mathematical physics. His address was impressive by reason of the elegance and precision of his statement. Not a word was wanting, not a word was in excess; never an error, an obscurity, or an ambiguity. markable also was the exactness of his calculations, -a matter of extreme difficulty to laymen. The whole material arranged itself before the eyes of the class in the form of a nicely adjusted masterwork of scientific art, so that every part exerted its full effect on the others, and to witness one of his deductions was a real æsthetic enjoyment. The complete understanding of his reasoning on these most difficult subjects implied, of course, some knowledge of the mathematical language which was his vehicle of thought; and it might happen, and did in fact sometimes happen, that a hearer could not comprehend why Kirchhoff made this particular deduction and not some other; but every one was able to follow his course of thought, consider it, and render it correctly. So that, paradoxical as it may appear, it was not impossible, without having really understood Kirchhoff, to reproduce his lectures from the notes into a respectable book. Kirchhoff was able to give his lectures uninterruptedly in Berlin for nine years. But we who heard him could remark the effort they caused him, and how he had to husband his strength. Yet he was always punctual, and the quality of his teachings was never depreciated. Finally, in 1884, the doctors forbade him to read; and although he was able to resume this his favorite occupation for a time, it was evident that his nervous system was shattered."

Kirchhoff was about fifty years old when he was called to Berlin. He had already done his greatest work on the spectrum, and published it. But his eyes had suffered from an accidental exposure to the sun, and his foot had been seriously injured in a way which impaired his general health. After 1882, the date of his Abhandlungen, he published a few papers.

Helmholtz, already quoted, writes: "Whether life in Berlin is favorable to scientific pursuits may well be doubted. The teacher, it is true, gains a wider, richer field of activity, but the investigator is robbed of a larger part of his time. Kirchhoff, however, was protected by his physical disability against most of the drive of the capital, and was able to labor as he had usually done."

In his power of handling physical problems, Professor Tait ranks him as the compeer of H. L. F. Helmholtz, Stokes, Sir William Thomson, and Clerk Maxwell. His discovery of spectrum analysis is an epoch-making one in science, felt equally in the humblest chemical analysis and in the remotest star and nebula.

#### BALFOUR STEWART.

To have achieved a permanent place in the literature of physics is no small achievement. This honor we feel that the world will accord to Professor Balfour Stewart. He was born in Edinburgh on November 1, 1828, and died on December 18, 1887. He pursued his studies at the Universities of St. Andrews and Edinburgh. Unlike most men who have devoted themselves to science, he did not linger in the shade of university walls, but began life in a mercantile office. It is said that his leaning toward physical science first strongly manifested itself on a business voyage to Australia, thus affording another instance of the effect of solation, so characteristic of sailing voyages, upon a philosophic temperament. His first scientific papers were published in the Transactions of the Physical Society of Victoria, in 1855, at the age of twenty-seven, and were entitled "On the Adaptation of the Eye to different Rays," and "On the Influence of Gravity on the Physical Condition of the Moon's Surface." It is curious to notice that these early papers were upon the subjects which were destined to engross his attention in mature life, - the subjects of light or radiant energy in general, and the effect of gravitation potential on the physical properties of matter. Shortly after his return from Australia, he abandoned business pursuits and became the assistant of Professor Forbes. In 1858 he enunciated his extension of Prévost's Law of Exchanges, and had the good fortune to express one of the great laws of nature in so simple a manner, and with such convincing proofs from his own investigations, that the future student will always connect it with the name of Balfour Stewart. Prévost had shown that a hot iron ball, for instance, surrounded by other objects, gained or lost heat in proportion to the absorbing and radiating power of the iron and the neighboring objects. Its temperature might remain constant if the heat it received from these objects compensated for that it lost to them. Stewart showed that radiation was not a mere surface phenomenon, — that there was a flow of heat from layer to layer of the particles of a body, — in other words, that there was a flow of heat pervading all matter, and that its direction and amount were determined by molecular conditions,— there being a complete equality between the absorbing and the radiating power of each substance. For his researches on this subject, he was awarded the Rumford Medal by the Royal Society.

In 1859 Balfour Stewart was appointed Director of the Kew Observatory, and for eleven years devoted himself to meteorology. The account of his labors in this new field can be found in the Reports of the British Association, and cover a great number of subjects, including the testing of thermometers, the perfection of self-recording apparatus for the study of the magnetism of the earth, similar apparatus for the study of atmospheric electricity, and the determination of the freezing point of mercury and the melting point of paraffine, with the subsidiary researches on the constants of the many forms of meteorological instruments.

In 1870 he was appointed Professor of Physics in Owens College, Manchester, a position which he held till his death. The character of his mind as an investigator was clearly shown by his advocacy of the laboratory method of instruction in physics. Although he was no longer in vigorous health, having been the victim of a frightful railroad accident, he did not shrink from the serious increase of labor which the laboratory method entails over the lecture and recitation method. His treatise on Practical Physics is one of the best laboratory treatises in physics, and forcibly illustrates the peculiar quality of the author's mind, which was marked by a philosophical breadth in the choice of methods to cultivate the scientific instinct.

By the publication of elementary treatises on Heat, on Practical Physics, on Elementary Physics, and on the Conservation of Energy, Stewart contributed largely to the cause of scientific education. Among these treatises, that on Heat easily takes the first place from a scientific point of view, and can be entitled a classic. It is probable that the general reader of science first gained his ideas of the great generalization of the conservation of energy from Stewart's simple exposition of the subject. He was also a frequent contributor to "Nature," and other scientific periodicals, and he wrote an article on Terrestrial Magnetism for the Encyclopædia Britannica. He also wrote, in conjunction with De la Rue and Loewy, a series of papers

on Solar Physics. It was natural that his labors as director of a meteorological observatory should attract his attention to even geological speculation, and we find several papers by him on Geology. In a late article in the Philosophical Magazine, he discusses the various theories which have been propounded to account for the magnetism of the earth, and puts forth the theory that it may be due to electrical currents circulating in the upper regions of the atmosphere, — the phenomena of the aurora being the discharge from the earth to the upper regions, or the discharge from the upper regions to the earth, — thus giving evidence of electrical currents. His paper in conjunction with Tait upon the heating of a disk of metal or ebonite by rapid rotation in vacuo is very suggestive in reference to the motion of heavenly bodies through space, and seems to afford color to the hypothesis of the dissipation of energy.

The closing period of his life was marked by that indulgence in peculiar physical speculations which were perhaps the outcome of a Scotch theological and philosophical environment. In "The Unseen Universe," and in the "Paradoxical Philosophy," both of which were written in conjunction with Professor Tait, we find an interesting expression of the thoughts which labors in a laboratory cannot fail to excite in a physicist's mind. The Unseen Universe is a valuable contribution to modern theological speculation, and affords the believer in miracles and the resurrection grounds for his belief, in the facts and great hypotheses of physical science. The evidence thus presented for a belief is especially interesting when compared with the historical evidences. The authors affirm, "As one result of this inquiry, we are led by strict reasoning on purely scientific grounds to the probable conclusion that a life for the unseen, through the unseen, is to be regarded as the only perfect life."

It is curious to reflect that the country which has produced a Reid and a Dugald Stewart now expresses its highest philosophical thought, not in metaphysics, but in physics. The student can find ample illustration of this in the writings of James Clerk Maxwell, of Sir William Thomson, and of Balfour Stewart.

#### BERNHARD STUDER.

PROFESSOR BERNHARD STUDER was born at Buren, near Bern, in August, 1794, and died at the ripe old age of ninety-three in the city of Bern, Switzerland, on the 2d of May, 1887.

He was educated as a clergyman, but never entered the ministry. After studying at the University of Göttingen, Studer became so in-

tensely interested in geology, that he resolved to consecrate all his life to the hard work of trying to disentangle the very complicated geological structure of his native country, the Oberland or Bernese Alps. His first work, as a sort of preliminary, was his "Monographie der Molasse," published in 1825. Considering the time and the state of palæontological knowledge, Studer showed capacity of the first order as a minute, diligent observer, and great skill for generalization, on a practical geological question, very little understood until his monograph.

Then Studer commenced in earnest his exploration of the Alps of the Valais, Vaud, Fribourg, Bern, and Lucerne, publishing excellent descriptions of the different large massifs of the Grand Saint-Bernard, of Monte Rosa, of the Simplon, St. Gothard, the Bernese Oberland, the country between the lakes of Thun and Lucerne, and his great work on the Swiss Occidental Alps, with a most important Atlas, Leipzig, 1884.

It can be said of him that he is the first geologist who has delineated and fixed the theory of *massifs* of the Alps, explaining them by the eruptive forces. Studer opposed sternly the opinions expressed lately by Ed. Süss of Vienna, and remained to the last a partisan of the Von Buch theory.

His "Geologie der Schweiz," in two volumes, Bern, 1851-53, is one of the best résumés ever published of the geology of a whole country,—clear, exact, well balanced, and extremely just towards all his contemporaries and brother geologists of the Alps and the Jura. In connection with this masterly work, Studer published, with his friend Arnold Escher von der Linth, "La Carte géologique de la Suisse," in four sheets; and a reduction in one sheet, two years later, 1855. The part of Escher von der Linth relating to the Geology of the Eastern Alps of Switzerland and Voralberg is on a level with Studer's researches; and his extremely difficult studies of the area of the cantons of Uri, Unterwalden, Schwytz, Glaris, and St. Gall can compare with the most complicated stratigraphy ever published in any country.

In 1859, Studer, entirely by his own exertions and direct influence, obtained from the federal government of Switzerland the organization of the Geological Survey, in view of publishing a Geological Map of Switzerland on the scale of 1:100,000. Studer was appointed President of the Commission, and until the last day of his life he directed the work admirably, and succeeded almost in bringing it to its close, for he saw the proof of the last sheet of the "Carte géologique de la Suisse" colored on the topographical map of General Defour, shortly before his death.

Studer was an excellent organizer, and he did a great deal as such, first at the University of Bern, then at the federal Polytechnic School of Zurich, and also as Director of the Geological Survey.

Short in stature, — he was called among his friends and contemporaries "le petit Studer," — of alender frame, and light-footed, he was one of the best Alpine climbers. He associated or got help from all the geologists who studied the Alps and the Jura. Being very honest and free in his opinions, he gave every one his due, and at the same time kept pace with all the progress that was made. At first Studer opposed the glacial theory of Venetz, De Charpentier and Agassiz; but, after several years spent in a close study of the question in the field, he became converted, and was afterward one of the most diligent propagators of the new doctrine.

He had the reputation of being an excellent friend, and quite witty, like his celebrated cousin, the minister Bitzius (Jeremy Gotthelf) of the Emmenthal, the author of the "Miroir des Paysans," the "Nouvelles Bernoises," and of so many remarkable novels on the life of the Bernese country people. Studer used to say, "Ce qu'il y a de plus remarquable dans Lyell, c'est Lady Lyell," — a compliment which highly pleased Sir Charles, who clapped his hands, the first time he heard it, exclaiming, "True! true!" But the witty remark applied exactly to himself, for Mrs. Studer was also a very remarkable lady in more than one sense. Neither Lyell nor Studer had any children, and they were able, with the great help of their wives, to consecrate all their time and life to the study of Geology.

With him disappears the last illustrious savant of the second generation of great geologists, who have built Geology up little by little. Studer came after Humboldt, Von Buch, Friesleben, William Smith, Alexandre Brongniart, Prévost, Cordier, D'Omalius, De Charpentier, De la Bèche, Conybeare, Buckland, etc., and from 1825 to 1880 he maintained his position as one of the best practical geologists in a time when they could point to such men as Élie de Beaumont, Sedgwick, Lyell, Murchison, Brown, Goldfuss, Frederic A. Romer, Alcide d'Orbigny, De Verneuil, D'Archiac, Agassiz, Barrande, Jules Pictet de la Rive, Boué, Escher von der Linth, Oswald Heer, Thurmann, etc.

Studer was present at the first meeting of the Society of the Swiss Naturalists (Société Helvétique des Sciences Naturelles) at Geneva, on the 6th of October, 1815, and he enjoys the unique distinction of having been a member during seventy-two years of the first association ever founded for the advancement of science.

Since the last Report, the Academy has received an accession of four members, A. L. Rotch, George F. Swain, Elihu Thomson, and Crawford H. Toy, all as Resident Fellows. The list of the Academy, corrected to date, May 29, 1888, is hereto added. It includes 178 Resident Fellows, 99 Associate Fellows, and 64 Foreign Honorary Members.

# LIST

## OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to May 29, 1888.)

#### FELLOWS. - 176. RESIDENT

(Number limited to two hundred.)

CLASS I. — Mathematical and Physical Sciences. — 76.

#### SECTION I. - 6.

# Mathematics.

Gustavus Hav. Boston. Benjamin O. Peirce. Cambridge. James M. Peirce, Cambridge. John D. Runkle, Brookline. T. H. Safford, Williamstown. Edwin P. Seaver. Newton.

#### SECTION II. - 12.

Practical Astronomy and Geodesy. J. Ingersoll Bowditch, Boston. Seth C. Chandler, Cambridge. Alvan G. Clark. Cambridgeport. George B. Clark, Cambridgeport. J. Rayner Edmands, Cambridge. Henry Mitchell, Nantucket. Edward C. Pickering, Cambridge. John Ritchie, Jr., Boston. William A. Rogers, Waterville, Me. Edwin F. Sawyer, Cambridgeport. Arthur Searle. Cambridge. O. C. Wendell, Cambridge.

#### SECTION III. - 43.

# Physics and Chemistry.

A. Graham Bell, Cambridge. Clarence J. Blake. Boston. Francis Blake, Weston. John H. Blake. Boston. Josiah P. Cooke, Cambridge. James M. Crafts, Boston. Charles R. Cross. Boston.

William P. Dexter. Amos E. Dolbear, Thos. M. Drown, Charles W. Eliot, Moses G. Farmer. Thomas Gaffield. Wolcott Gibbs. Frank A. Gooch. Edwin H. Hall, Henry B. Hill, N. D. C. Hodges. Silas W. Holman, William L. Hooper, Eben N. Horsford, T. Sterry Hunt, Charles L. Jackson, William W. Jacques, Alonzo S. Kimball. Leonard P. Kinnicutt, Worcester. Joseph Lovering. Charles F. Mabery, Arthur Michael, Lewis M. Norton. John M. Ordway, William H. Pickering, Cambridge. Robert H. Richards, Edward S. Ritchie, A. L. Rotch, Stephen P. Sharples, Francis H. Storer. Elihu Thomson, John Trowbridge, Cyrus M. Warren, Harold Whiting, Charles H. Wing, Edward S. Wood,

Roxbury. Somerville. Boston. Cambridge. Eliot, Me. Boston. Newport, R. I. New Haven. Cambridge. Boston. Salem. Boston. Somerville. Cambridge. Montreal. Cambridge. Newton. Worcester. Cambridge. Cleveland. Boston. Newton. New Orleans. Boston. Brookline. Boston. Cambridge. Boston. Lynn. Cambridge. Brookline. Cambridge. Boston. Cambridge.

#### SECTION IV. - 15.

# Technology and Engineering.

George R. Baldwin,
John M. Batchelder,
Chas. O. Boutelle,
Winfield S. Chaplin,
Eliot C. Clarke,
James B. Francis,
Lowell.

Gaetano Lanza, Boston. E. D. Leavitt, Jr., Cambridgeport. William R. Lee, Roxbury. Hiram F. Mills. Lawrence. Alfred P. Rockwell. Boston. Charles S. Storrow. Boston. George F. Swain, Boston. William Watson, Boston. Morrill Wyman. Cambridge.

# CLASS II. — Natural and Physiological Sciences. — 49.

#### SECTION I. - 8.

# Geology, Mineralogy, and Physics of the Globe.

Thomas T. Bouvé, Boston. Algernon Coolidge, Boston. William O. Crosby, Boston. William M. Davis, Cambridge. O. W. Huntington, Cambridge. Jules Marcou, Cambridge. William H. Niles. Cambridge. Nathaniel S. Shaler, Cambridge.

# SECTION II. - 6.

#### Botany.

William G. Farlow,
George L. Goodale,
H. H. Hunnewell,
Charles S. Sargent,
Charles J. Sprague,
Sereno Watson,
Cambridge.
Cambridge.
Brookline.
Boston.
Cambridge.

#### SECTION III. - 19.

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